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CONTENTS

177 Editor's Note/L. A. UTRACKI

178 Introductory Remarks/GEORGE L. BATA

179 M. R. PIGGOTT/Fiber-Matrix Interactions

189 A. GARTON/Characterization of the Interface: Some Initial Results for Mica-Polypropylene Composites

193 L. A. UTRACKI and B. FISA/Rheology of Fiber- or Flake-Filled Plastics

212 I. LEE, S. TURNER, and R. T. WOODHAMS/Hot-Rolling and Forging of Mica-Filled Polyolefins

218 M. FENTON and G. HAWLEY/Properties and Economics of Mica-Reinforced Plastics Related to Processing Conditions

230 J. P. TROTIGNON, B. SANSCHAGRIN, M. PIPERAUD, and J. VERDU/Mechanical Properties of Mica-Reinforced Polypropylene Composites

239 D. SANTRACH/Industrial Applications and Properties of Short Glass Fiber-Reinforced Plastics

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EDITOR'S NOTE

In the Industrial Materials Research Institute of the National Research Council of Canada (IMRI-NRCC), the three areas of plastics activities are of special interest: polymer blends, reinforced plastics and composites, and mathematical modeling of plastics processing and properties. To support these activities, IMRI organizes and hosts annual mini-symposia on each of the three subjects. The proceedings of the first symposium, "Polyblends-81," and of the related meeting on thermodynamics of liquids were published in *Polymer Engineering and Science*, [**22**, (1981)]. The current issue contains the papers presented during the first symposium of the second series, "Composites-81," held in Montreal on December 8, 1981. The first symposium of the third series was held on February 9, 1982, and the texts are in the final stage of preparation for publication in *Polymer Engineering and Science*

The mini-symposium "Composites-81," being the first on the subject, was organized and sponsored by IMRI with a specific goal in mind: to review the current status of knowledge in the area of plastics composites containing short fibers or flakes. An effort was made to secure the balanced input from both academia and the plastics industry.

There were seven 45-minute-long presentations. First, the matrix-filler interactions were discussed for fiber (M. R. Piggott) and mica-reinforced plastics (A. Garton). Both authors presented their most recent results. The review of the melt flow of polymers filled with short fibers and flakes (L. A. Utracki and B. Fisa) was illustrated with the authors' results on polyethylene-mica system. Processing, application, and properties of mica-filled plastics were discussed as follows: calendering and properties of oriented mica-composites were considered by R. T. Woodhams; the influence of the type of mica, its preparation and treatment on the properties of mica-filled plastics, as well as the economics of mica reinforcing were debated by the two co-authors, M. Fenton and G. C. Hawley; the mechanical properties of injection-molded mica-filled polypropylene were discussed by B. Sanschagrin. Finally, the application, processing, and economics of use of the short glass fibers were reviewed by D. Santrach. After each of the presentations, a general discussion was held; transcripts of these are being published at the end of each appropriate paper.

L. A. Utracki
Guest Editor

INTRODUCTORY REMARKS

Last night, I looked at some of my old books. I have been active in this field for a little over 35 years now. I started my work with phenolic plastics, as well as with fiber- and paper-reinforced laminates. Thumbing through the pages, these books make some interesting reading in today's context, as they are dated 1946, 1947, and 1950. One of them says that, while information has been accumulated during the past 30 years concerning the manufacture and properties of reinforced plastics, no coordinated account has been available to the interested student. Then, I look at a book that recently came out written by one of our common friends, and it says that the field of fiber composites has developed rapidly over the last 20 years and that no material scientist should now be without a working knowledge of it. Better late than never. This means that, for about 60 years, we have been pushing on the same wagon wheel, hoping to understand what happens.

In one of the old books, I read that "the combination of a fabric with a resin produces a type of material the mechanical properties of which are strikingly different from those of either," and then the new book says that "the properties of the composite may bear little relation to those of the components." Both books give a list of applications for composites: 30 years ago it was aircraft, today it is airframes, motorcars then, now it is ground transport, boat decks before, now it is marine applications, chemical industry then, now chemical plants, building industry, now buildings, and so on. Not much seems to have changed. The only change in applications I have noticed is that, about 30 years ago, we were worrying about the furniture industry and bearings as an application; these uses seem to have gone out the window now. They are replaced by medical devices and sporting goods. There are some major advances, though. I read in the book published in 1947 that the ratio of modulus to tensile strength is 1.6 but, looking at the new book, I notice that the "value of practical strengths" is stated to be about 1/15th of the Young's modulus. Are things improving? Either our tensile strength is going down, or the Young's modulus is going up, but if neither did, then at least we express them now in GPa and not in kg/mm^2—and this is in itself an improvement.

I counted the number of equations: there were 17 equations in my old book, which is about the same thickness as the new one with 330 equations. One's first impression could be that maybe we are as ignorant as ever but that we are expressing it a lot more quantitatively.

Nevertheless, being quantitative permits us to describe increasingly more complex structures, makes possible the modeling of the behavior of the material under loading, and it helps us to predict future performance. Being more quantitative is a good thing after all: it enables us to identify and separate out our variables and leads to a better understanding of the relationships between structure and properties—and this is basically what the science of composite materials is about.

It appears, then, that we may well, after all, be making some progress in the right direction.

We organized this mini-symposium to help you to help us. We will be asking you to help us define the field of applied research to which we should be contributing, to help us to better define our specific objectives, and also to give us feedback from time to time, as to whether we are going in the right direction. I hope that we will succeed in establishing this line of communication with you and that this meeting will be only the first of a series of mini-symposia to follow.

I thank you for coming here to work with us, and I would like to wish you a good conference.

George L. Bata, Director
Industrial Materials Research Institute
National Research Council Canada

Fiber-Matrix Interactions

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The mechanical properties of short, fiber-reinforced polymers are governed as much by the interface as by the properties of fiber or polymer. Interface properties of importance include adhesion and radial and longitudinal (frictional) stresses. These directly govern strength, modulus, and toughness of the composite and indirectly affect the resistance of the composite to environmental influences, such as water. These interface properties and the resulting interactions under applied stresses are examined and their influence on mechanical properties is discussed.

INTRODUCTION

A fiber composite is effective because the stress is transferred from a weak and highly flexible plastic to very strong and very stiff fibers. Common sense suggests that, for the stress transfer to take place effectively, the adhesion between fibers and matrix needs to be good. However, in practice, stress transfer is a very complex process and depends on a number of other factors, in addition to adhesion.

Simple calculations show that, when a fiber composite is stressed, very large shear stresses are present at the fiber-matrix interface, especially near the fiber ends (1). Experimental studies confirm the presence of these stresses and show that they are even higher than simple theory suggests (2). Thus, when a fiber composite is tested to destruction, we expect the adhesion between fibers and matrix to fail long before the composite fails. This is so even when the adhesion is as good as it possibly can be; i.e., when the adhesion strength is greater than the polymer matrix strength. When adhesion has broken down, stress transfer can still take place through frictional slip. The matrix extends more than do the fibers, due to its lower modulus. Thus, slip occurs near the fiber ends. This slip process is very important, not only for reinforcement, but also for resistance to cracking.

In this article, the effects of adhesion and shears arising from slip are discussed.

ADHESION

Fibers used in composites normally have a coating ('sizing') on them. This has two purposes. One is to prevent fiber-fiber contacts, which cause cracking of the fibers and weaken them. The other purpose is to promote adhesion. The fiber supplier uses different sizings for different matrices, and the sizing is designed to give good adhesion for the particular fiber-matrix combination being considered.

For glass fibers, to be used in epoxies, polyesters, and other polymers, the sizing usually contains a silane adhesion promoter. This usually consists of an organic part, such as an allyl group, which interacts and bonds with the polymer, attached to a silane functional group, which adheres to the glass. The compounds used for polyester and epoxy are different. The exact nature of the silane used is normally a trade secret.

Much confusion and uncertainty surrounds the exact nature of this adherend-adhesive bond. Claims in favor of significant amounts of covalent bonding should not necessarily be taken at face value. Theories of bonding and experiments with glass fibers (and bulk glass) are critically reviewed by Plueddemann (3). He considers that, while the chemical bonding theory is the most plausible theory of bonding for glass, hydrogen bonding between silanols of the coupling agent and glass surface is the predominant mode of reaction, rather than covalent bonding. Other secondary bonding forces, such as Van der Waals forces, may also be important, with other fibers.

Even the seemingly well-established contact angle approach, using Young's equation, has a very serious fundamental problem. Thus, *Fig. 1* suggests that, for a drop in equilibrium on a solid surface, and having a contact angle θ,

$$\cos\theta = (\gamma_{sg} - \gamma_{sl})/\gamma_{lg} \qquad (1)$$

Here the γs are interfacial energies, and the subscripts g, l, and s refer to the media at the interface, g being gas, l, liquid, and s, solid (4).

The problem, of course, is that, if the diagram were correct,

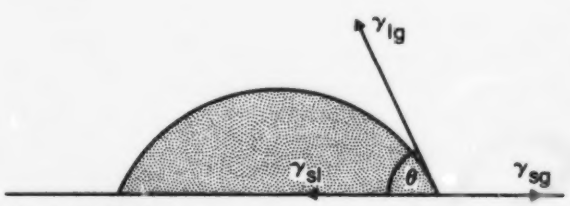

Fig. 1. Sessile drop.

$$\gamma_{lg} \sin \theta = 0 \quad (2)$$

and either $\theta = 0$ or $\gamma_{lg} = 0$. Since θ is often observed to be greater than zero, and $\gamma_{lg} \neq 0$, we must conclude that $\gamma_{lg} \sin \theta \neq 0$, and the surface must be deformed around the rim of the drop by this force normal to the surface (5). Consequently, the real θ is not the same as the θ normally observed and measured. Another problem is that γ_{lg} and θ are the only parameters that can normally be measured.

Much confusion also surrounds the surface and interfacial energies of solids. Surface energy in solids only manifests itself in cleavage, flow, mass transport, and other non-reversible phenomena. Elastic extension involves no surface work. The surface energies of solids can be related to the interatomic bond strengths through the modulus of elasticity. A simple treatment of this (6) suggests that these surface energies are in the range + 0.05 to + 5 Jm^{-2} for metals and inorganic crystals and perhaps somewhat less for plastics, due to their lower Young's moduli. The theoretical value for iron of 1.5 Jm^{-2} is compatible with values obtained from cleavage experiments at very low temperatures; i.e., 1.36 Jm^{-2} (7). These conditions ensured almost no plastic work.

With glass, which can undergo very little plastic deformation, experimental values for γ_{sg} from the usual type of cleavage experiments carried out at 20°C (i.e., 3.5 to 5.3 Jm^{-2} (8)) are much greater than those obtained by methods involving no significant plastic work; i.e., 0.5 to 1.0 Jm^{-2} (9). This difference has been shown to arise from plastic deformation at the crack tip in cleavage experiments (10). Thus, cleavage experiments aimed at giving realistic surface energies are difficult to devise and carry out because of the need to prevent plastic deformation. In addition, almost complete exclusion of the atmosphere is necessary, and experiments should ideally be carried out close to O K in ultra-high vacuum. This is because, normally, the surfaces of all solids are covered with many layers of adsorped materials; e.g., o_2, N_2, H_2O, etc. These layers form very quickly when new surfaces are produced and can only be removed with great difficulty (e.g., high-temperature treatment in ultra-high vacuum). Their presence reduces the energy required to make new surfaces.

Contact angle measurement does, however, provide a useful indication of compatibility between adhesive and adherend. A contact angle close to zero shows that they can be brought into close contact, so that Van der Waals and other secondary bonding forces become significant. This, together with mechanical keying effects, seem to be the most likely agents accounting for adhesion in systems involving nonmetals.

(With pairs of metals, on the other hand, extremely good bonds can be obtained. The metal atoms can be brought to within normal interatomic distances at the interface, so that the metallic (electron cloud) bond can be formed. The only weakness arises from oxide inclusions. This type of bonding requires pressures high enough to cause extensive plastic deformation and redistribution of the surface material but can be carried out at 20°C.)

Since polymers are held together, to a large extent, by secondary bonds and mechanical keying, it is possible to produce a bond with a glass fiber that is as strong as the polymer itself. It is essential, however, that the adhesive have a strong polar group (e.g., a silane) that has a strong affinity for the glass and is not easily displaced by water, for which glass also has a strong affinity.

In the case of carbon fibers, the surface is much more inert than glass, and bonding is much weaker. In this case, much more reliance is placed on mechanical keying. The surface is roughened and made more chemically active by etching with strong acids, or oxygen at high temperatures, and proprietary adhesion promoters are then coated on the surface.

In the case of Kevlar, adhesion promoters are used for combination with epoxy resins, but none are used with polyesters.

INTERFACIAL STRESSES

The shear stresses at the interface, τ_i, govern the slip process. τ_i, in turn, is the product of the interfacial coefficient of friction, μ, and the normal (radial) compressive stress at the interface, which is equivalent to a pressure at the interface, P.

With reinforced thermosets, this pressure, P, is generated by the shrinkage of the resin during cure. With thermoplastics, which are molded at high temperatures and used at much lower temperatures, P is produced by the differential thermal shrinkages of matrix (high coefficient of thermal expansion; typically, 500 to 1000 μK^{-1}) and fiber (low coefficient of thermal expansion; radial thermal expansion coefficients are: Kevlar, 59 μK^{-1}; carbon, 8 μK^{-1}; and glass, 15 μK^{-1}).

Friction arises from two processes: asperities on one surface ploughing up the other surface, and extreme heat and pressure caused by the sliding resulting in local welding of asperities. A simple theory suggests that the coefficient of friction for combinations of deformable materials should be approximately constant, since it is roughly equal to the ratio of the shear strength to the yield pressure of the softer material (11). In practice, coefficients of friction can range from 0.04 for aluminum on ice (12) to ~ 100 for pairs of clean hot metals in high vacuums (13). Coefficients of friction can be quite low for some polymers and ceramics (< 0.1) and quite high for rubbers (> 1), while clean metals usually have intermediate values (0.6 to 1.2).

MEASUREMENTS OF INTERFACIAL PROPERTIES

Single-fiber pull-out tests are the normal method of measuring the interfacial properties. The results are usually plotted in the form of pull-out force *vs.* embedded length; see *Fig. 2.* (14).

It is observed that fibers can be pulled out in one piece as long as the length is less than some critical value. For a fiber of diameter d, and strength σ_{fu}, the slope of the graph *(Fig. 2)* (M, say) gives the interfacial

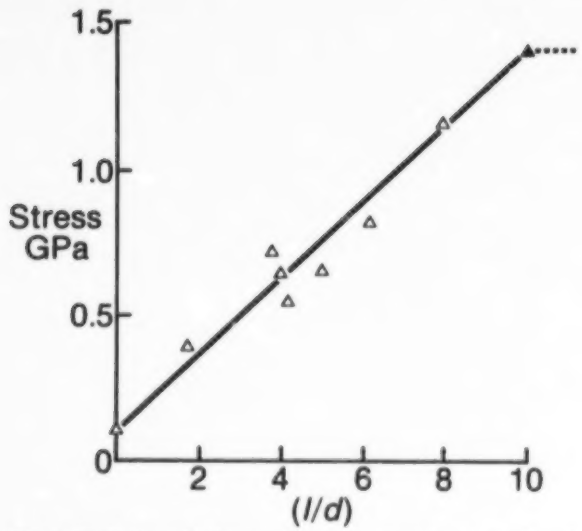

Fig. 2. Typical results from pull-out experiments. At lengths of 10 cm or more, the fibers broke.

shear stress. Thus,

$$\tau_i = M/\pi d$$

and the maximum force gives the fiber strength,

$$\sigma_{fu} = F_{max}/\pi d^2$$

The critical length, L_c, is a very important parameter. Note that

$$L_c/d = \sigma_{fu}/4\tau_i$$

$2L_{cf}$d is the critical fiber aspect ratio. If a fiber with this aspect (length/diameter) ratio is completely embedded in a plastic, and the plastic is then stretched, the fiber can be broken. A shorter (lower aspect ratio) fiber embedded in the same plastic cannot be broken, no matter how high the stress on the plastic is. Instead of breaking very short fibers, the polymer slides past them until its ductility is exhausted, and the polymer then fractures.

The pull-out experiments measure τ_i but give no direct information on P or μ. These parameters can be measured by pulling fibers out of matrices that are subject to known stresses. This has so far only been done on model systems with steel fibers (15). With a polycarbonate matrix, $P = 7$ MPa and $\mu = 0.6$; with epoxy, $P = 3.0$ MPa and $\mu = 0.19$. (These single-fiber models gave values for P that are rather low. The accepted value for carbon-fibers-reinforced epoxy is about 20 to 30 MPa based on a coefficient of friction of about 0.3 and a frictional shear stress of 6.0 to 8.6 MPa (16). When fluorocarbon release agents were used, μ was reduced to 0.12 for polycarbonate and 0.10 for epoxy.)

These experiments also gave information about the strength of the adhesion. With the polycarbonate, it reached and appeared to slightly exceed the shear strength of the polymer; i.e., 55 MPa. After being pulled out, the wires still had pieces of the polymer adhering to them. With the epoxy, similar results were obtained. When the wires were coated with fluorocarbon release agent before embedding in the polycarbonate, the adhesive strength was reduced to 1/40 of its normal value. The reduction was only five-fold when fluorocarbon-coated wires were embedded in the epoxy.

A method of measuring adhesion using specially shaped pieces of polymer with one fiber embedded in it has also give useful practical results (17). Polyester-glass adhesion strengths were in the range 1.5 to 7 MPa, while epoxy-glass adhesion strengths were between 15 and 30 MPa. The shear strengths of the interfaces were greater than these (tensile) strengths. Coupling agents improved the adhesion strengths in the case of the polyesters, but not in the case of the epoxies.

COMPOSITES WITH ALIGNED FIBERS

No experiments on well-characterized systems (i.e., those where P and μ are known) appear to have been carried out. Thus, we can only describe theoretical work.

The most easily treated system is that where all the fibers have the same aspect ratio, s, and are parallel. When stressed in the fiber direction, the fiber-matrix interface (or the matrix near the interface) is expected to fail when the strain, ϵ_l, reaches the value ϵ_{ls} where, for moderate to high fiber loadings

$$\epsilon_{ls} \simeq \sigma_{mu}/\sqrt{E_f E_m} \qquad (3)$$

where σ_{mu} is the ultimate tensile strength of the polymer matrix and E_f and E_m are the fiber and matrix Young's moduli. The applied stress corresponding to this strain is σ_{ls}, where

$$\sigma_{ls} \simeq \{V_f E_f (l - \sqrt{E_m/E_f}/s) + V_m E_m\}\epsilon_{ls} \qquad (4)$$

and V_f and V_m are fiber and matrix volume fractions. (These equations are approximate ones; fuller equations are available elsewhere (18, 19)).

Composites are usually designed for a strain of 0.001 or 0.002. For glass-fiber-reinforced plastics, ϵ_{ls} is typically 0.005; for Kevlar it is 0.004, and for stiff carbon, 0.0022. Thus, the design strain has to be exceeded before slip can take place in perfectly adhering systems.

However, if, due to a design oversight (e.g., some unexpected stress raiser), these values are exceeded, slip will occur near the fiber end. This is not serious, so long as the aspect ratio exceeds the critical value, s_c. The composite can then be stressed to much higher stresses and will not fail until the ultimate stress, σ_{lu}, is reached:

$$\sigma_{lu} \simeq (V_f(l - s_c/2s) + V_m E_m/E_f)\sigma_{fu} \qquad (5)$$

Since P is expected to be about 25 MPa, and μ is expected to be about 0.3, s_c is typically 150 to 200. Thus, 10 μm diameter fibers only have to be 1.5 to 2 mm long to exceed the critical aspect ratio. If they exceed 5 cm, the aspect ratio effect becomes negligible ($s_c/2s << 1$), and *Eq* 5 gives about the same result as the Rule of Mixtures expression:

$$\sigma_{lu} = V_f\sigma_{fu} + V_m\sigma_{mu} \qquad (6)$$

The Young's modulus of the composite is quite close to that given by the appropriate Rule of Mixtures expression:

$$E_l = V_f E_f + V_m E_m \tag{7}$$

so long as $s >> \sqrt{E_f/E_m}$. For glass, s need only be 55 or more; for Kevlar, s should be 70 or more and, for stiff carbon, s should be 130 or more in order to satisfy this criterion.

Typical theoretical stress-strain curves for carbon-fiber-reinforced epoxies are shown in *Fig. 3*. For $s < s_c$ (e.g., $s = 100$) the fibers are not expected to break, and the curves have been terminated at a strain 1 percent. The slip point is at the upper end of the dashed line. *Fig. 4* shows the corresponding plots for modulus and strength *vs.* fiber aspect ratio.

These curves were drawn on the assumption that the adhesion was perfect. However, reducing the adhesion strength to 1000th of its maximum possible value has only quite a small apparent effect; see *Fig. 5*. (When the adhesion parameter, a, is 1.0, the adhesion fails when the interfacial stress at the fiber end reaches the ultimate shear strength of the matrix. When $a = 0.001$, it fails instead at 1000th of this value.)

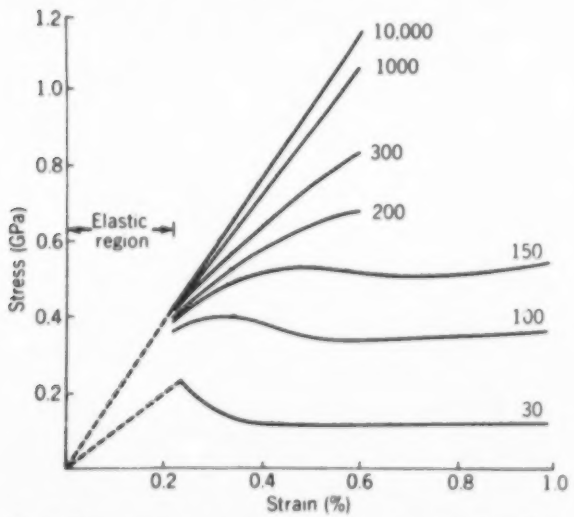

Fig. 3. Stress-strain curves predicted for aligned carbon-fiber-reinforced epoxy resin with $V_f = 0.5$, for different fiber aspect ratios, with perfect adhesion between fibers and matrix (18).

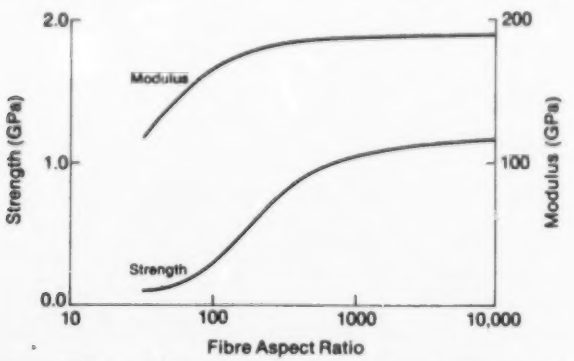

Fig. 4. Effect of fiber aspect ratio on composite strength and modulus.

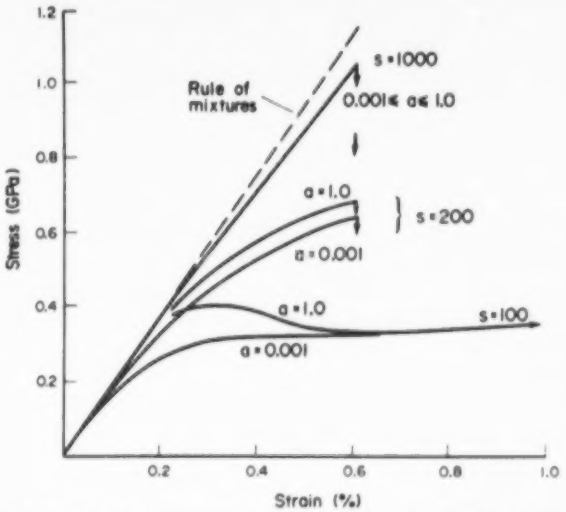

Fig. 5. Effect of adhesion on stress-strain curves predicted for carbon-epoxy of Fig. 3. a = adhesion parameter, s = aspect ratio (18).

The most important effect of poor adhesion is that it reduces the stress and strain at the slip point. Thus,

$$\epsilon_{ls} \simeq a\sigma_{mu}/\sqrt{E_f E_m} \tag{8}$$

and this reduced strain gives a corresponding reduction of stress, as given by *Eq 4*.

The radial stress and coefficient of friction also affect the properties, especially for small aspect ratios, since they control s_c. *Figure 6* shows the effect of coefficient of friction for the same carbon-fiber-reinforced epoxy as for *Figs. 3* and 4, with $s = 200$. As expected, higher coefficients of friction reduce s_c, and so bring the curves closer to the Rule of Mixtures value. The effect of radial shrinkage stress is more complex; see *Fig. 7*. This is the same composite as before, with $s = 200$. Note that there is a severe decrease in stress at the slip point

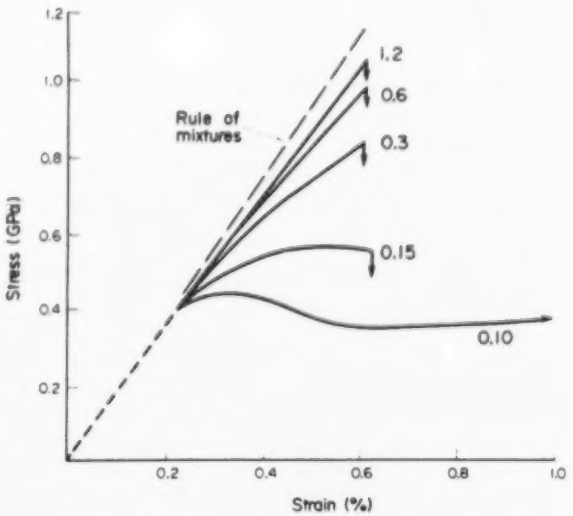

Fig. 6. Effect of fiber-matrix friction coefficient on stress-strain curves predicted for carbon-epoxy of Fig. 3. Fiber aspect ratio = 200 (18).

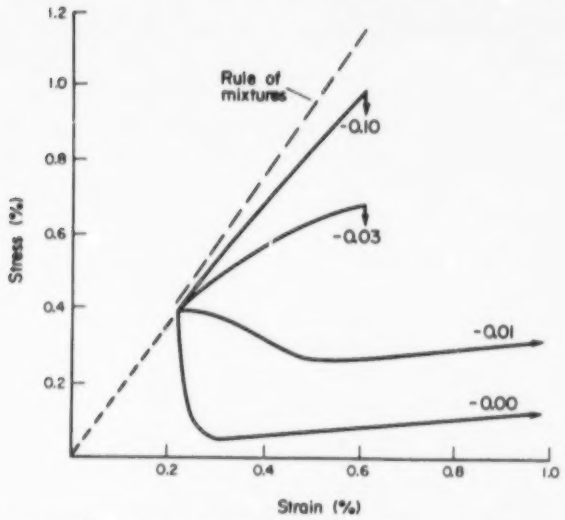

Fig. 7. Effect of matrix shrinkage stress on stress-strain curves for carbon-epoxy of Fig. 3. Fiber aspect ratio = 200. The figures on the curves indicate P values (18).

when $P = 0$. Failure is likely to occur with such a composite as soon as slip starts. It is important to observe that the combination of poor adhesion and small P is likely to be particularly harmful.

There is good evidence (20, 21) that poor adhesion has an adverse effect on the compressive strength of aligned fiber composites; see *Fig. 8*. In addition, it reduces the off-axis properties (i.e., the strength transverse to the fibers) and the shear strength. With glass-fiber-reinforced plastics, good adhesion is vital for resistance to environments such as water. Note that, if fiber slip takes place in an otherwise well-made and carefully used composite, the slipped regions can be

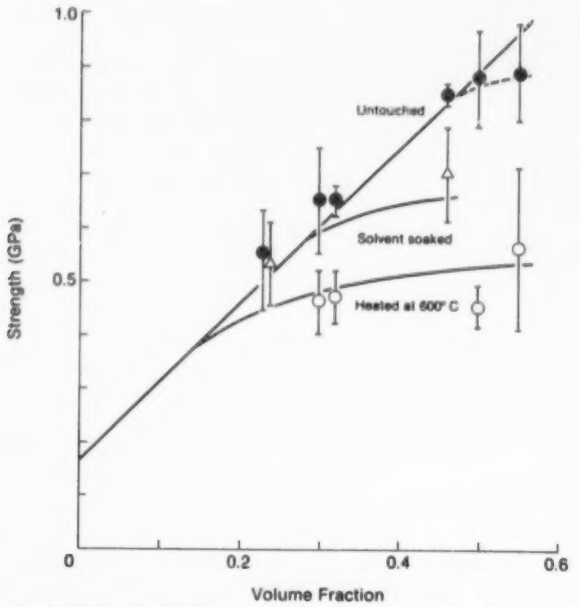

Fig. 8. Effect of various fiber surfaces treatments on compression strength of aligned glass-fiber-reinforced polyester resin. Heating at 600°C removed the adhesion promoter (21).

infiltrated with water, which then has an ideal base for further attack on the interface. Thus, glass fiber composites should not be stressed beyond the slip point.

Toughness depends on sliding. Fibers pulling out at crack faces can contribute greatly to the work of fracture and, hence, prevent cracking or reduce the damage sustained on impact. For increased toughness (22), we can 1) use fibers having the critical aspect ratio, as indicated in *Fig. 9;* 2) use large-diameter fibers, or make many fibers (e.g., in a tow or roving) cooperate and extend the interface work over a long distance from the crack face, but fail near the crack face (as shown in *Fig. 10*) (the work of fracture is proportional to the effective

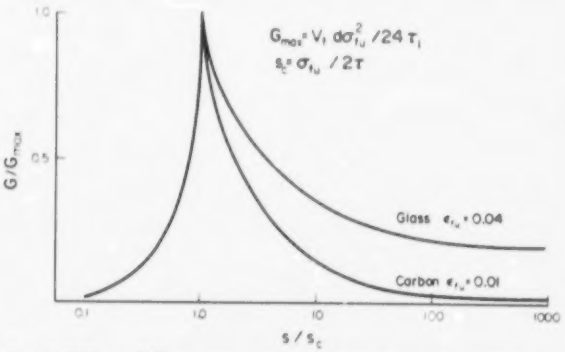

Fig. 9. Effect of fiber aspect ratio on toughness in composites. dimensionless curves can be used to predict toughness for all aligned, uniformly strong fiber systems.

Fig. 10. Toughening by the use of fiber bundles. They fail near the crack face, but extend the interface work over a long distance.

diameter), or 3) reduce the shrinkage stress of the polymer. Recent tests indicate that method #3 may be particularly suited to reducing the brittleness of aligned, continuous carbon-fiber composites; see *Fig. 11*.

RANDOM SHORT-FIBER COMPOSITES

When short fibers are randomly directed in a composite, the modulus of the composite is usually moderately higher than that of the plastic alone, but the strength is often less. This is because it is difficult to get efficient packing of randomly oriented fibers, so that fiber volume fractions are generally small. *Fig. 12*, taken from some work with Portland cements and concretes (23), shows that the maximum fiber volume fraction is about 6 percent when the fiber aspect ratio is 100, corresponding to a fiber length in the case of glass of about 1 mm. At such low fiber volume fractions, stiffening is marginal:

$$E_c \simeq 0.2\ V_f E_f\ (1 - \sqrt{E_f/E_m}/s) + V_m E_m \qquad (9)$$

where E_c is the composite Young's modulus. For example, for glass in a polyester matrix having a modulus of 3.0 GPa, E_c = 3.7 GPa.

Nor is very great strengthening obtained. The theoretical maximum strength for a composite with random fibers having aspect ratios less than the critical is σ_{cu}, where

$$\sigma_{cu} \simeq 0.2\ V_f \tau_i s + V_m \sigma_{mu} \qquad (10)$$

(This is the formula for the aligned fiber case (17), modified for random fibers using the orientation factor of 0.2 (19)). For τ_i = 9 MPa and σ_{mu} = 70 MPa, this comes to about 80 MPa, a 14 percent increase. By using shorter fibers, higher volume fractions can be achieved. Such composites have higher moduli but lower strengths. This is the case with glass-filled polyester resin premixes, where V_f is in the range 0.2 to 0.4, the modulus is usually between 7 and 17 GPa, and the strength is 21 to 70 MPa. In this case, the composite is actually weaker than the unreinforced matrix.

More stiffening can be obtained with carbon fibers. The stiffest of these have Young's moduli of about 400 GPa, so the composite modulus (*Eq 10*) can be 6.5 GPa. However, as with the glass fiber premixes, there is a high probability of composite failure at low stress because of the slip at the fiber-matrix interface. A carbon fiber oriented along the direction of the applied stress will stretch an amount 0.9 μm, while the matrix will have stretched at least 6 μm when the composite stress reaches 40 MPa. Other fibers, less favorably oriented, will have stretched much less. These internal voids will promote early matrix failure.

For long fiber, we can calculate a minimum volume fraction for reinforcement, V_{fmin}, using the formula (24)

$$V_{fmin} = \frac{E_f \sigma_{mu} - E_m \sigma_{fu}}{(\chi_l E_f - E_m)\sigma_{mu}} \qquad (11)$$

Here, χ_l is an orientation factor, which is 0.2 for the random fiber case. For glass, $V_{fmin} \simeq 0.17$ percent while for carbon, $V_{fmin} \simeq 15$ percent for randomly oriented fibers. (For Kevlar, it is about 0.12 percent). In the case just discussed, $V_f < V_{fmin}$ for glass (and Kevlar) and $V_f < V_{fmin}$ for carbon.

For randomly oriented fiber composites, it is advantageous to have s_c as small as possible, since we are obliged to use fibers with small aspect ratios in order to achieve reasonably high fiber volume fractions. Thus, we need to have the matrix shrinkage stresses as large as possible and to have a high coefficient of friction at the fiber-matrix interface. In addition, the adhesion should be as good as possible, so that slip and separation do not occur at low stresses. These composites cannot be very tough because of the low fiber content.

Sheet-molding compounds, where the fibers can usually be assumed to be coplanar but randomly oriented in the plane of the sheet, give similar results, except that the orientation factor χ_l = 0.375, and the fiber volume fractions for high aspect ratios can be much higher. The expression for modulus (e.g., *Eq 9*) is

$$E_l = 0.375\ V_f E_f + V_m E_m \qquad (12)$$

For composite strength, the equation usually assumed for the planar random case

$$\sigma_{cu} = 0.375\ V_f \sigma_{fu} + V_m \sigma_{mu} \qquad (13)$$

in analogous with the formula for modulus.

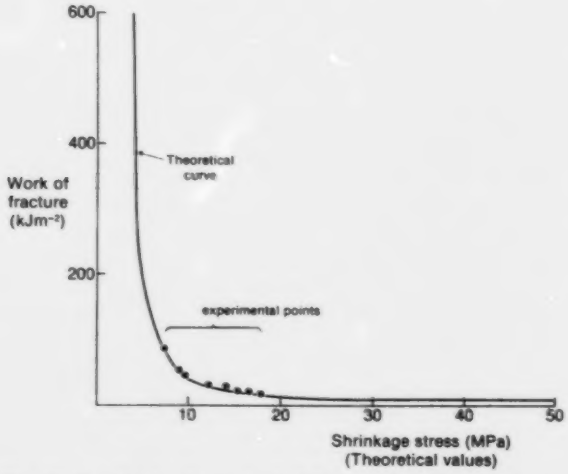

Fig. 11. Toughening by control of the matrix shrinkage stress.

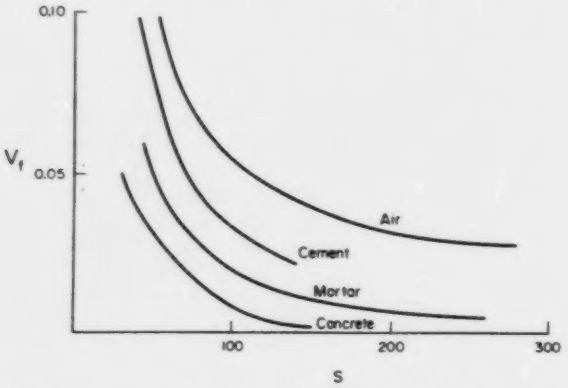

Fig. 12. Maximum fiber volume fraction vs. fiber aspect-ratio for fibers directed randomly in three dimensions (23).

An approximate theory for the stress-strain curve suggests that nonlinear effects should be observed when the fibers are quite short, as with aligned fibers; see, e.g., *Fig. 3*. It also suggests that the Poisson's ratio in the plane of the sheet should be quite close to 0.5, except at very low volume fractions.

The composite breaking strength is predicted to be a little less than that given using *Eq. 13*, however; the slip theory (25) gives (26)

$$\sigma_{lu} = 0.318\ V_f \sigma_{fu} (1 - s_c/2s) + V_m \sigma_{mu} \qquad (14)$$

The difference between the constants used in *Eq. 13* and *14* is not very great. *Equation 14* is, however, more complete, since it includes the fiber aspect ratio effect.

The short fiber case ($s < s_c$) cannot, at present, be described by such simple equations as these.

CONCLUSION

The mechanical properties of fiber composites depend on the interface as much as on the nature of the fiber and matrix. If the fibers are short, composite strength and modulus depend critically on having an interface that can transmit the stress, even when regions near the ends of the fibers slide slightly within the matrix as stress is applied. When the fibers are long, conditions at the interface are less critical for strength and modulus, but are extremely important for toughness. Here, control of fiber sliding is necessary in order to prevent the composite being too brittle. The adhesion between fibers and matrix plays a secondary role. Good adhesion is necessary in aligned fiber composites to ensure good off-axis properties. It is also important for the resistance of the composite to various environment factors. Thus, for example, water can penetrate the composite and weaken it if adhesion is poor, especially when the fibers are glass.

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DISCUSSION

L. P. Blanchard. When you start to pull, some of these fibers are strong enough to resist. Maybe they do break in some cases only. Do you not think that you are actually getting a flow of the plastic around the fiber instead of pulling the material apart. If the plastic is actually melted to the surface, there should be a fairly good adhesion. Are we pulling the plastic off the fiber or are we having the plastic flow around the fiber as the fiber moves down through the stress? This was something that you talked about, as of rubbing, ruggedness, and things sliding, slipping over, welding of joints and things like that, breaking of these welds . . . I wonder if this occurs that close to the surface, or whether flow takes place a little further. If we examine the fibers after pulling out, we may be able to see. You might find the answer there.

M. R. Piggott. We found that a steel fiber pulled out of a polycarbonate matrix had little bits of plastic on it. Undoubtedly, there was some sort of matrix failure there. We concluded, also, that in certain cases there was a little bit of matrix plastic flow. In the main, the surface was clean, which seems to indicate that most of what we measured was friction. We are presently doing some work in which we are pulling single 20μm glass fibers out of polyester resins. *Fig. 1* shows the type of result we are getting. Here again, we do occasionally get a little bit of plastic attached to the fiber after pull-out. The attached plastic gives a very large plowing component to the frictional force (friction is partly plowing and partly shearing). The large plowing effect gives a large coefficient of friction. We think that, when we pull on an embedded fiber, it shrinks significantly. This encourages the failure of the bond because the interface then has a tensile stress, as well as a shear stress. It could be that this shrinkage also reduces slope of the pull-out curve, since it would reduce the shear stress. As we pull a fiber out, the force required is decreasing all the time; i.e., the fiber shrinkage is decreasing, so that the slope of the end of the pull-out curve gives the interface shear stress without any effects due to fiber shrinkage.

It is very difficult to do the experiment because, with glass, we must only embed perhaps two or three mm. With carbon, it is even more difficult because the em-

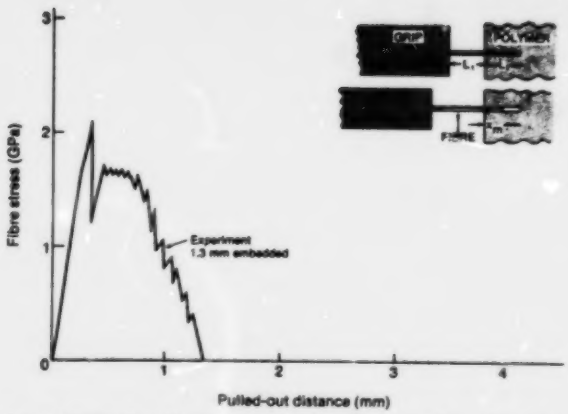

Fig. 1. Typical pull-out curve obtained with a 20μm-diameter glass fiber, embedded in a polyester resin.

bedded length must be even less, and they are very brittle fibers that break very easily. We have not succeeded yet, but we already have many results with glass that need to be interpreted.

G. L. Bata. It looks like what you need is a curiy fiber.

M. R. Piggott. Oh yes, this principle is used, of course, with reinforced concrete. However, in fiber composites, although this would permit good stress transfer from matrix to fibers, it could have a bad effect on toughness by reducing the amount of fiber pull-out work.

R. T. Woodhams. There are some interesting characteristics of fibers that we should bring out. We observed them during the studies carried out and never reported. We have been trying to compare the performance of glass fibers with polyester fibers and nylon fibers. The reason for this was to check the effect of fiber roughness; when we talk about reinforcing fibers, you nearly always talk about graphite or Kevlar or glass, and always there are some comments about the roughness of the fiber and questions about how it affects the pullout energy. We compared cord (i.e., twisted filaments that have a rough surface) with straight fibers. We expected that, because of the rough surface of the cord, there would be greater mechanical interlock; we would get a greater fracture energy. However, we found that the cords tended to give a lower fracture energy than rovings, which consisted of parallel filaments bonded together. Of course, when you talk about the fracture energy proportional to diameter, you know that you cannot get fibers of all diameters. So you take rovings and use a binder to hold the individual filaments together and, in this manner, you can make a variety of diameters and lengths. For these systems, you will find that the fracture energy increases with diameter; you would like to get your reinforcing fibers as nice, big rods. But if this means that your critical aspect ratio now has to be maybe 12 in., you are not going to extrude that. So there is a practical upper limit to the critical length that you could employ; that is usually about 1/4 or 1/2 in. The polyester or nylon fibers are better because they will flow and conform through the mixing and molding process without breaking, whereas glass fibers will break and, in addition, they cause a lot of abrasion. Now, returning to our experiments: we used a hot-air dryer to blow the polyester or nylon filaments through a column. They were heated up to their softening point for about a fraction of a second, and then the individual filaments started to relax at the ends. This way, you make nobby fibers, fibers that have an enlarged ends like a dumbbell. We thought, gee, that is great! However, when we incorporated these into plastics, we found that the fracture energy went down markedly; we locked the fibers rigidly into the matrix so they could no longer be pulled out. The Izod fracture energies were quite small. It indicates the fact that Mike brought out: that, for maximum fracture energy, you want frictional energy. As a number of people have shown, it is the largest part of the fracture energy; you want the fiber long, you want the diameter large, and then the length should be near the critical length. I should also point out that, if you put these fibers in something brittle, like concrete, 1 percent by weight of fibers will increase the fracture toughness by a factor of 200. You do not see much in the way of strength or modulus, because these are not effected very much, but you can get phenomenal increase in fracture toughness with relatively small concentrations of fibers, which are not difficult to incorporate.

L. A. Utracki. A couple of years ago, Czarnecki and White (*J. Appl. Polym. Sci.*, **25**, 1217 (1980)) investigated glass, polyaramid, and cellulosics fiber damage during the processing. They observed a periodic type of deformation due, not to mechanical but to rheological forces. In the process, the rigid glass fiber would break, polyaramid would form kinks with a period of about 100μm, and the most flexible cellulosic fiber, would adopt a helicoidal structure. How could we turn this seemingly natural phenomenon to profit?

M. R. Piggott. I cannot comment on that, it sounds like a very interesting result.

L. A. Utracki. How do you correlate the θ-wetting angle measurements, which are done at high temperature, using solid fiber or flake and molten polymer, with the performance of the solid composite?

M. R. Piggott. You cannot relate them directly. If you get good wetting at high temperature and then you cool it down, you may have brought the materials close together on an atomic scale. This is the main condition for forming a good bond. The surface energy of a solid may not be at all related to how well they stick. Surface energy is a measure of how strongly the atoms or molecules are attracted together inside the material, since it can be related to the attraction between the atoms or molecules at the surface and those inside. It does not tell you too much about how they would be attracted to other materials. In adhesive bonds, there are problems in developing theoretical relationships because of the interfacial layers that are between the two materials, so I do not see how you can relate θ directly to bond strengths or composite behavior at all, I am afraid.

L. A. Utracki. The only correlation one gets is empirical.

M. R. Piggott. Absolutely, empirical. I think that, in the case of reinforced polymers, this does not matter a great deal. To take an extreme case: if you want a strong bond between a hard solid and diamond, you must have covalent bonds across the interface, since diamond is covalently bonded. In the case of metal, you can easily get an excellent bond. You take two metals and clean their surfaces so that there is virtually no oxide, and you deform them really well in pressing them together. What you find is that you get atomic contact between the two different metals and you get a bond that is as strong as the metal. In the case of diamond, I do not think that we know how we could get the covalent bond needed, say, from diamond to alumina. In the case of bonding plastic to glass, in the absence of deleterious environments such as water, all that is needed is to get the materials close together on an atomic scale, this will give the necessary secondary bonding effect. The bond can be Van der Waals, or it can be polar, but whatever the origin, it is a secondary bond. However, these types of bonds can be just as strong as the polymers themselves because polymers are only held together by secondary bonds.

In short, I see big problems of adhesion in ceramic and metal composites. There, you have to find ways of making sure that you do get primary bonds. In the case of reinforced plastics, you do not need primary bonds and, as long as you get a low contact angle, which indicates that you are getting the two materials close together, you will get the secondary bonding effects needed to give good stress transfer, in the absence of aggressive environments.

L. A. Utracki. I detest to disagree with you. If what you said would be true, all the work on sizing of mineral fibers and flakes would be pointless. You, yourself, said that you have to have proper sizing for proper polymers. I do not know if sizing provides primary or secondary bonding, but it is very important to have good adhesion, especially in the perpendicular direction; your ϵ_1 may not depend on it very strongly, but ϵ_2 and ϵ_3 in your treatment will. Your treatment must take into account the sizing effect, the type of bonding between matrix and fillers.

M. R. Piggott. I do not think we disagree. I think that one needs the sizing in order to provide a material that is compatible with the glass and at the same time compatible with the polymers. For example, we had to stick gelatine to cellulose acetate. These are completely incompatible materials, so we provided an interfacial zone that had compatibility with both. This was obtained by using a solution of cellulose acetate in acetone with a suspension of gelatine. This was coated onto the film. The cellulose acetate from the solution was attracted to the cellulose acetate film base, and the gelatine in suspension was attracted to the gelatine in the layer. In this way, we obtained good bonding. Silane, or whatever other agent is used, behaves similarly; these materials have a group that is attracted to the polymer. It is a compound having one end like the glass and one end like the polymer. Work on sizings is very important because of the need to develop interfacial zones of compatibility that can withstand environmental effects.

D. Santrach. We are buying this very expensive chemical, silane from Union Carbide at $25.00 a kilo—quite expensive for us. What does it do? Basically, it makes the glass fiber attractive to a polymer. In other words, it gives better wetting. If you provide a good interface for all practical types of resins, if you provide good dispersibility, this much contact will give good performance even if adhesion is very low. If you have a lot of intimate contact, the composite will work.

M. R. Piggott. I think that the glass fiber industry is very successful in providing glass that adheres well to polymers. Our tests indicate that one can get interfacial strengths that are equal to the matrix strength without difficulty. With our steel fibers, we did it without using any coupling agent. Obviously, glass is different from steel, and with glass there is sufficient incompatibility that you need to provide something that bridges that compatibility gap.

The great tendency to theorize about interfacial bonding has always bothered me. Chemical bonding in homogeneous materials is an extremely complex subject, as every second-year student of chemistry knows, and much remains to be done before it is fully understood. Chemical bonding between unlike materials across an interface is even more complex, and we have hardly even begun to develop the tools needed to deal with it theoretically. Experiment in this area is extremely difficult, since a surface is normally quite different from the bulk material, due to the presence of difficult-to-remove surface oxygen, nitrogen, and water, etc.

L. A. Utracki. My feelings are that there are many different mechanisms involved. In sliding, for instance, you mentioned that, after treating the fiber with fluorinated hydrocarbons, the strength dropped drastically. This obviously indicates that you have broken the interaction between matrix and the fibers. On the other hand, there are a number of indications, very similar to what Ray was saying, where the failure is in the matrix; the polymer fails *not* at the interface between the matrix and fiber. There are a number of different mechanisms involved, described by different relations.

R. T. Woodhams. I am working predominantly in the random rather than unidirectional fiber distribution. Here, the variables are very complex. Would you just touch on the critical aspect again? Could you redefine that, as it might relate to what happens when you go into a random structure? You said that the strength may drop as one gets at an angle on some of these fibers.

M. R. Piggott. On adhesion, I would recommend Bikerman's book (ref. #5 in my article). When the adhesive bond is about equal to the matrix strength, the failure does not necessarily follow the bond line. Instead, it goes into the matrix. He advances a simple theory that explains why this happens. Turning to critical aspect ratio, this is the fiber strength divided by twice the interfacial shear stress, τ_i. Suppose we take the fiber strength as 2 GPa, which is a typical value for glass, carbon, or Kevlar, and τ_i = 10 MPa. This gives a

typical critical aspect ratio of 200. In a short-fiber composite, the aspect ratio may be as small as 30; i.e., a long way below the critical. Theoretical analysis for the random composites has not yet satisfactorily described the case of fibers with less than the critical aspect ratio. I can draw stress-strain curves for composites with fibers with the critical aspect ratio. (I have been working on this in the last week or two). I get the results indicated in *Fig. 2*, which show stress-strain curves for various aspect ratios. Above the critical value, these curves are very similar to what you previously saw for long fibers (*Fig. 3* in my article) with failure at the breaking strain of the fiber. The failure strain for composites with fibers having aspect ratios less than the critical value is difficult to predict. Experimental results indicate that failure takes place when the composite strain is less than the breaking strain of the matrix. It has been suggested that this may be due to cracks developing near the fiber ends. However, the experimental evidence in favor of this is not conclusive, and since the local tensile strains in the matrix near fiber ends are kept small by adjacent fibers, such cracks seem unlikely to form or propagate. In addition, such a process takes no account of the large effect of the adhesion between fibers and matrix. Thus, we can draw stress-strain curves, such as those shown in *Fig. 2*, but for fiber aspect ratios less than the critical, and for fiber volume fractions less than the minimum for reinforcement, we cannot predict the composite failure strain, at present. It will be affected by such factors as fiber volume fraction, matrix ductility and work of fracture, fiber-matrix adhesion, and relative stiffness of fiber and matrix. Composites with moderate fiber volume fractions could well fail when the matrix "lets go" of the fibers completely, and starts to slip past them continuously. This occurs at a strain given by $\epsilon_{1p} = 2s\tau_f/E_f$ for aligned fibers. In *Fig. 2*, the curves for the smaller aspect ratios ($s < s_c$) have been terminated at the point where the matrix slips past all fibers with misalignments not exceeding 35° from the direction of the applied stress. It can be seen that the strengths predicted for low aspect ratios are thus quite small.

Strengths less than the unreinforced matrix strength are obtained with molding compounds, as a glance at the *Plastics Encyclopedia* shows. However, even very short fibers give moduli that are an improvement on the unreinforced matrix, and they also improve the thermal stability of the plastic. The theoretical modulus is given by the slope of the curves in *Fig. 2*. Notice that the modulus decreases as the applied stress is increased, except in the case of the infinitely long fibers.

R. Woodhams. How this depends on the fiber angle?

M. R. Piggott. The curves in *Fig. 2* are for the random fiber case. When the fibers are aligned, and the composite is stressed at an angle to the fiber direction, the composite failure can be determined from the critical stress criterion, or the Tsai-Hill criterion (1). Both criteria can be applied to short, aligned-fiber composites, and predict a very rapid decrease in composite strength as the angle between the applied stress and the fibers is increased.

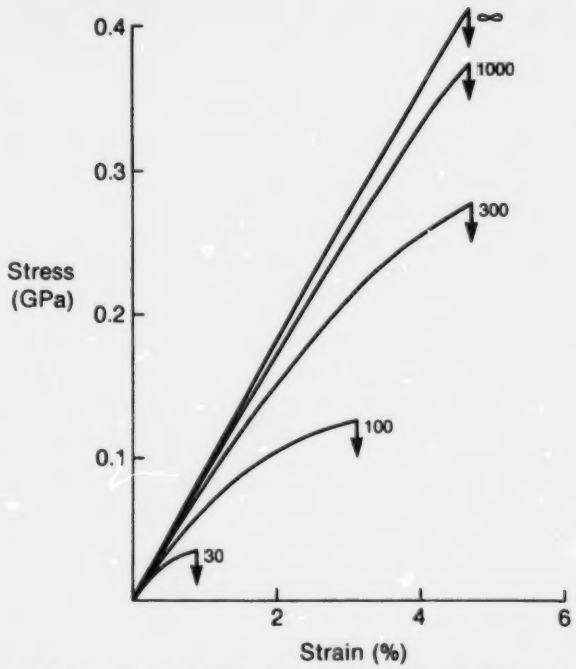

Fig. 2. Theoretical stress-strain curves for short, randomly oriented, glass-fiber-reinforced polymer sheets. The figures on the curves denote the fiber aspect ratios. The critical aspect ratio is 300.

Reference (1). M. R. Piggott, "Load Bearing Fiber Composites," p. 75, Pergamon, Oxford (1980)

L. P. Hebert. I have a question concerning spiropolymers. How is this work coming along?

M. R. Piggott. This work progresses relatively slowly, since we have to synthesize our own polymers. We have shown that the special polymers reduce the shrinkage stress, and thus increase the toughness of the carbon-fiber-reinforced composite. We got something like a five-fold improvement with pultrusions, and verified that the improvement in toughness was obtained without any loss of shear strength. We are having problems making prepreg tapes, however, since for these we need to develop a two-stage curing process. In addition, the monomers are highly susceptible to water.

Characterization of the Interface: Some Initial Results for Mica-Polypropylene Composites

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Preliminary results are presented that demonstrate that the chemical and physical structure of the polypropylene at the mica-polypropylene interface can be markedly different from that of the bulk polymer. This results from the ability of the mica to nucleate the crystallization of polypropylene, from the adsorption of polar impurities onto the mica surface, and from the effect of the mica surface on degradation reactions, particularly with chlorinated hydrocarbon coupling agents.

INTRODUCTION

It is frequently stated that the interface between the reinforcement and the polymer matrix is crucial in determining the useful properties of polymer composites, yet very few techniques are available to characterize the interfacial region without interference from the bulk polymer and from the reinforcement. One area of considerable progress has been the application of a variety of spectroscopic techniques (1-5) to characterize either the surface of the reinforcement or the bonding between the polymer and the reinforcement. Most of the effort in this area has been applied to thermosetting polymer matrices because of their use in high-performance composites (e.g., in aerospace applications) and because chemical changes in the matrix can be followed relatively easily, at least in the early stages of the cure. The purpose of this brief communication is to describe some recent progress in characterizing the interface in mica-reinforced polypropylene. This composite material is typical of a range of low-cost, reinforced thermoplastics that are finding an increasing number of high-volume applications, particularly in the transportation industry.

POLYPROPYLENE MORPHOLOGY AT THE INTERFACE

It is immediately obvious by optical microscopy (*Fig. 1*) and by differential scanning calorimetry (DSC, *Fig. 2*) that mica (Suzorite H200 mica platelets) nucleates the crystallization of polypropylene (Monomer Polymer Laboratories, isotactic, 400,000 molecular weight, antioxidant free). Micrographs 1a and 1c (*Fig. 1*) were taken at 200°C and show the location of the mica flakes dispersed in molten polypropylene between cover glasses (6). The temperature was then reduced to 125°C, and the crystallization of the polymer, followed by viewing between crossed polarizers, when the mica and the molten polymer are invisible and the growing spherulites appear as light areas on a dark background. It is clear from *Fig. 1b* that crystallization occurred preferentially on the surface of the mica platelets.

This observation was confirmed by DSC (*Fig. 2*), which shows that the mica displaced the polymer crystallization exotherm to appreciably higher temperatures. Note that it was necessary to mix the mica thoroughly with the polypropylene powder in the DSC pan before melting to obtain reproducible DSC data. When a very small particle-size mica (e.g., Suzorite 325 HK)

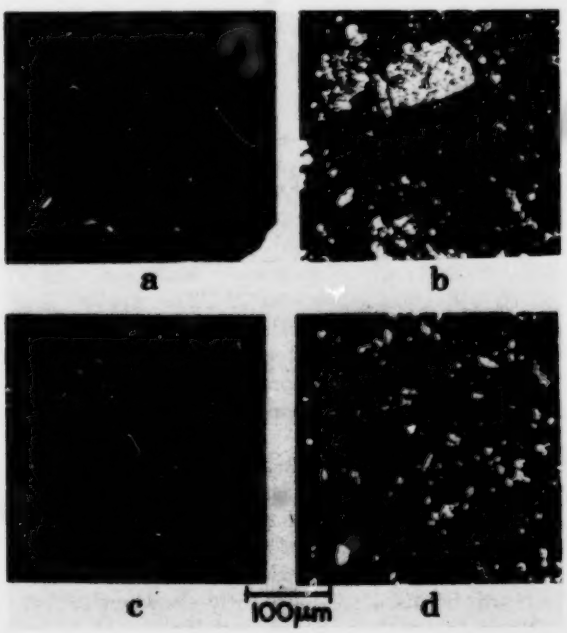

Fig. 1. Crystallization of polypropylene in the presence of mica flakes. (a) (b) polypropylene + untreated mica; (c) (d) polypropylene + silane treated mica. Micrographs (a) and (c) were taken at 200°C to show location of the mica flakes. Micrographs (b) and (d) show the same areas as (a) and (c), respectively, but were taken with crossed polarizers and show crystallization occurring at 125°C.

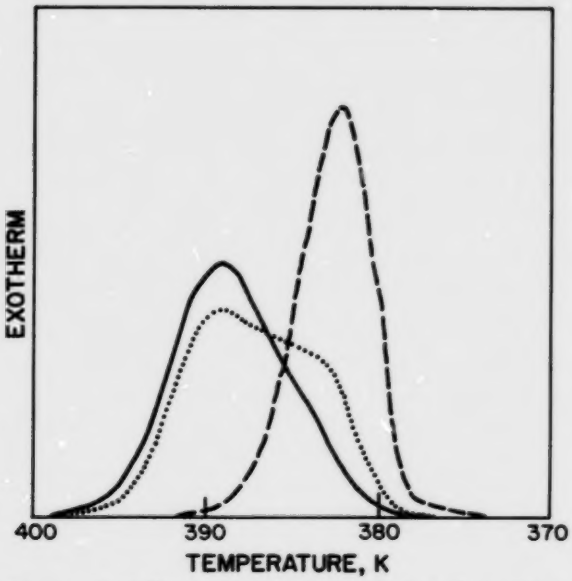

Fig. 2. Crystallization exotherms for mica/polypropylene thermal history: 5 min at 205°C then cooled at 10°C/min. Data normalized to constant weight of polypropylene. - - - - polypropylene; · · · · polypropylene + 21 phr mica; ——— polypropylene + 52 phr mica.

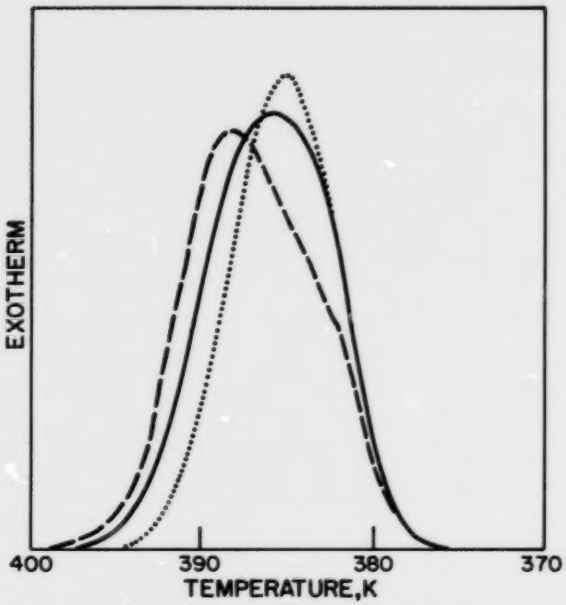

Fig. 3. Modification of crystallization exotherm by coupling agents. - - - untreated mica, 30 phr; ——— 2% chlorinated hydrocarbon blended with resin, 30 phr mica; · · · silane treated mica, 30 phr.

was used, an even dispersion was difficult to obtain by hand, and so the DSC results were less reproducible, making it necessary to prepare at least five separate samples before the data could be treated with confidence.

When the mica was treated with a silane coupling agent (Dow Corning 6032, applied from aqueous solution) the nucleation effect was greatly diminished. A comparison of *Figs. 1c* and *1d* demonstrates that nucleation occurred almost at random and not preferentially on the surface of the mica as is shown in *Figs. 1a* and *1b* for untreated mica. DSC provides support for this observation *(Fig. 3)*. The polymer crystallization was displaced to lower temperatures relative to the untreated mica. Similar behavior was observed for commercial-silane-treated micas. For example, for Suzorite 325 NP (which is identical to Suzorite 325 HK except for the application of an azo-functional silane) at 30 phr in polypropylene, the onset of polymer crystallization was 4°C lower than for equivalent samples containing untreated Suzorite 325 HK and the temperature of maximum exotherm was 5°C lower.

The blending of a chlorinated hydrocarbon wax with the polymer has also been shown to enhance the properties of mica-polypropylene composites (7-9). *Figure 3* shows that the presence of chlorinated hydrocarbons also inhibits the nucleating ability of the mica. These results will be discussed more fully elsewhere (6, 10).

Nucleation of the polymer crystallization at the mica surface will result in the morphology of the polymer at the interface being different from that of the bulk polymer. A transcrystalline (11) layer will result, which consists of closely packed columnar crystallites growing outwards from the surface. It has been argued, particularly by Schonhorn, *et al.* (12-14), that such a morphology will result in better adhesion between the polymer and the reinforcement, although others have argued that the effects of morphology are masked by chemical changes (e.g., oxidation) associated with the production of that morphology (15-17). It has, as yet, not been possible to conclusively separate the direct effects of morphology (e.g., the modulus and ductility of the interfacial polymer and the effect of morphology on adhesive forces) from the indirect effects of interface morphology (oxidation during fabrication, zone-refining of the interface by the growing crystallization front). Finally, the effects of shrinkage must be considered. Semicrystalline polymers shrink appreciably (~5 percent) on crystallization, and this shrinkage occurs in a period of only a few seconds, potentially setting up large stresses. If the interfacial polymer is a solid during the bulk of the crystallization process, as will occur with surface nucleation, the stresses are more likely to be concentrated at the interface than if the mica were surrounded by fluid, molten polymer as the shrinkage occurred.

CHEMICAL STATE OF POLYPROPYLENE AT THE INTERFACE

Direct chemical analysis of the interfacial polymer is difficult for polypropylene samples reinforced by mica platelets, because the interface cannot be examined in isolation. A model sandwich composite was therefore constructed by molding a thin layer (~100 μm) of polymer between two freshly cleaved sheets of muscovite mica. This composite could then be readily separated by immersion in cold water, thus exposing the interfacial material to examination. Both the mica surface and the polymer surface were then examined by the internal reflection spectroscopy (IRS) technique (6, 10, 18). This involves pressing the sample surface against a ger-

manium IRS element for infrared (IR) spectroscopic examination. The depth to which the surface is sampled depends upon the wavelength of the IR radiation but will typically be ~0.5 μm for the mid-IR range. By varying the angle of incidence of the IR beam or the refractive index of the IRS element, different depths of the surface may be sampled, enabling a concentration profile to be built up.

The example described here is the case where 2 percent of a chlorinated hydrocarbon wax (Chlorez 700, Dover Chemical Co.) was uniformly blended with the polypropylene prior to molding to improve coupling between the mica and the polypropylene (10). The sandwich composite was held for 4 min at 200°C before cooling, then separated with cold water. The IRS spectrum of the polymer surface then shows an intense absorption at 1650 cm^{-1} with a shoulder at 1740 cm^{-1} (*Fig. 4*). Comparison with reference spectra and work with model systems (10) indicate that these absorptions are due to olefinic unsaturation and halogenated carbonyl groups, respectively, as would be expected from the thermal degradation of a chlorinated hydrocarbon (19). When an IRS element of lower refractive index (KRS-5) was used, a greater depth of the surface was sampled (~5 μm), and the degradation product absorptions were appreciably less intense relative to the polypropylene absorptions (data not shown). When the polymer film was examined by transmission IR (thus sampling the total thickness), the degradation product absorptions were barely significant relative to the polymer absorptions (*Fig. 4*, inset). These observations indicate that the degraded chlorinated hydrocarbon was located preferentially in the 0.5 μm of the polymer adjacent to the mica surface. A precise calculation of the local degradation product concentration would require a more exact knowledge of the nature of the olefinic unsaturation, but a comparison with the spectra of reasonable models indicates that the level of unsaturation in the 0.5-μm-thick layer was $\geq$ 1 mole/kg and was at least 10 times the level in the bulk of the polymer.

The most likely explanation of this effect is the well-known catalytic effect of many inorganic compounds on the thermal degradation of chlorinated hydrocarbons (19). Adsorption of the chlorinated hydrocarbon onto the mica surface may also occur to some extent, and this will also serve to increase the local degradation product concentration. Separate experiments (10), however, indicate that the chlorinated hydrocarbon in its undegraded state is retained only weakly by the mica surface. Whatever the cause, it is clear that the chemical state of the polymer at the mica-polypropylene interface is markedly different from that in the bulk polymer.

CONCLUSIONS

The chemical and physical state of the polypropylene at the interface in mica-polypropylene composites is shown to be potentially very different from the state of the bulk polymer. Some techniques for characterizing the polymer at the interface are illustrated.

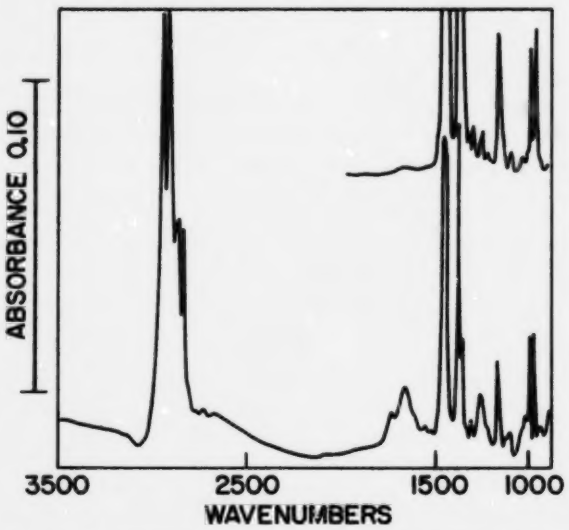

Fig. 4. IRS spectrum of polypropylene at mica-polypropylene interface. Inset is transmission spectrum of the same polymer scaled so that the polymer absorptions are of a similar intensity to the IRS spectrum.

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DISCUSSION

L. P. Blanchard. What do you believe is causing this breakdown of the Chlorez at the surface of mica?

A. Garton. In PVC degradation kinetics, the effect of inorganic species and polar surfaces is well-noted. I think we are looking at the same thing.

R. T. Woodhams. You showed an interesting slide to illustrate the fact that you could strip the mica off the polypropylene mixed with Chlorez by putting it in cold water. It shows that the presence of water will completely destroy the adhesion at the interface. In the handbook of adhesives, it is shown that, for most inorganic solids, conditioning in 100 percent relative humidity causes the surface energy of the solid to drop to about 22 ergs/cm^2. It is very low value, and there are very few polymers that will adhere to a surface with such a low surface energy.

A. Garton. With the proviso that it is possible for the moisture to get in there. This is not necessarily true for polypropylene.

R. T. Woodhams. Did you do the experiment with the silane as well as the Chlorez?

A. Garton. Yes, and we could not get it off as easily. This reflects the difference in susceptibility to moisture of these two surface active agents.

L. A. Utracki. How did you prepare the specimens? Was the Chlorez deposited on the mica directly as you did with silane?

A. Garton. The Chlorez was blended with the polymer, which is the normal procedure.

L. A. Utracki. So you observe preferential migration of Chlorez from the uniform blend.

A. Garton. Yes, that is true.

R. E. Prud'homme. When using this 6032 silane, you have the possibility of a reaction with the polymer. Do you believe that? Did other people try to create this reaction to improve the bonding between the silane and the polymer?

A. Garton. I have seen no evidence for the 6032 that it does actually graft to polypropylene, no.

L. P. Hebert. I am going to work on addition of metal filings to polyester. What would be the possible surface change at the interface?

A. Garton. Large. You are dealing with a surface which is very active. Unfortunately, it is rather difficult to look at the surface of a filing. I would start with a metal sheet.

L. A. Utracki. From the point of view of thermodynamics, the polymer should preferentially crystallize at the edges of mica flakes, as the surface potential of the edges is higher than of the slip plane. Did you see evidence of this?

A. Garton. There seemed to be some tendency for crystallization to occur at the edges, yes.

Rheology of Fiber- or Flake-Filled Plastics

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Thermoplastics and thermoset materials filled with inexpensive, mainly inorganic, particulates are an important class of engineering plastics. Here, the short fiber and flake fillers play a major role. In this paper, the melt rheology and processability of these resins is reviewed, and the flow behavior of mica-filled polyethylene is discussed in greater details.

INTRODUCTION

The increase in resin costs paralleled by a reduction of choice of polymers available on the market (1) forces the plastics industry toward diversification via alloying and reinforcing. The pace toward reinforced plastics accelerated considerably (2, 3) since 1975. The projected consumption of fillers and reinforcements by the North American plastics industry in 1990 is 6.7 million metric tons, giving about 30 percent of market share to filled or reinforced plastics. (In the text, the terms "filler," "reinforcement," and their corresponding derivatives will be used interchangeably).

There are two reasons for using the filled systems, the performance and the economics, (i.e., the cost effectiveness of these types of materials). It is known that one cannot obtain the same high performance from the pure polymer as from the reinforced system. The automobile application of reinforced plastics serves as an obvious example.

The usage and cost of the most popular fillers are listed in *Table 1*. It can be seen that the prices of these materials range from 0.5 to 3 ¢/in.^{3}, i.e., they are comparable to those listed for: polypropylene (PP), polyethylene (PE), polystyrene (PS), poly(vinyl chloride) (PVC), poly(ethylene terephthalate)(PET), and ionomer (1). This indicates that one should use fillers either with a more expensive resin or in order to achieve the properties of one. Examples of cost calculations can be found in Refs. 5 and 6; e.g., in blending of polyester with $CaCO_3$, one can reduce the final material and production cost by 17 percent. It is clear that the cost saving obtained on a per-volume basis is considerably less than that which is usually assumed. However, as the cost of feedstocks mounts and the resulting price of the basic resins increases, one should expect the use of fillers to become more and more attractive.

Table 1. Filler Consumption in 1979 (4)

Material	Usage 1000 tons	Costs (US cents) per pound	Costs (US cents) per in.^{3}
Calcium carbonate	1388	4 to 18.50	0.4 to 1.8
Talc	163	1.50 to 4.50	0.2 to 0.5
Clays	131	1.25 to 19	0.1 to 1.8
Silicas	50	20 to 32.50	1.9 to 3.0
Mica	14	6.75 to 18	0.7 to 1.9
Glass	12	26	2.3
Miscellaneous	176		
Total	1934		

In order to process the composites, it is necessary to know their rheological behavior. For practical reasons, the most interesting systems are concentrated suspensions in viscoelastic liquids; i.e., the systems that are most difficult to treat theoretically, whose rheological properties cannot be predicted.

In this article, we want to offer a perspective view of the flow behavior of filled polymer melts. In particular, the following subjects will be discussed:

- Interactions in filled polymer melts.
- Rheology of Newtonian liquid suspensions.
- Rheology of filled polymer melts.
- Processing and rheology.

The review will map the areas of rheological activity on filled polymer melts. We shall also try to indicate the uncharted domains awaiting exploration.

INTERACTIONS IN FILLED POLYMER MELTS

Interaction between the polymer matrix and particulate filler influences properties and ultimate usefulness of the finished product. Fillers that can be well-dispersed and strongly bonded to the matrix are sought after. Both the filler concentration and interactions alter the rheological and processing characteristics of the resin. In this section, the effect of filler-matrix interactions will be reviewed.

Polymer

Information about configuration of macromolecules in polymer melts has been generated by diffraction methods. Most authors had studied solid amorphous polymers containing a small fraction of tagged chains, which could be detected by X-ray or neutron-scattering methods. The most frequent conclusion is that the polymer consists of an assembly of interpenetrated random coils with dimensions comparable to those observed in theta solvents; e.g., Kim (7) reported (see *Table 2*) that for PS:

Table 2. Molecular Dimensions in Bulk Polystyrene (7)

$M_w \cdot 10^{-4}$	R_g (measured) (Å)	$10^3 \cdot R_g/M_w^{\frac{1}{2}}$ (Å)	R_g (calculated) (Å)	
			random coil	collapsed coil
4.1	86	0.425	56	32
9.5	141	0.457	84	43
16.3	157	0.389	110	51

$$R_g/M_w^{\frac{1}{2}} = \text{const.}$$

where R_g is the radius of gyration and M_w is the weight average molecular weight. Another proposed model is that of a collapsed coil (viz., last column in *Table 2*). The subject was reviewed by Graessley and more recently by de Gennes (8), who concluded that most of the experimental evidence is compatible with the random coil model.

Fillers

The most widely used mineral filler is $CaCO_3$, followed by talc, clay, silica, mica, and glass (10). These fillers represent a wide variety of shapes and particle sizes (*Table 3*). They all contain varying amounts of water adsorbed on the surface (11). Excepting the glass hollow microspheres, they have relatively high density ($\rho = 2.4 - 3.0$) which may limit their usefulness.

Filler-Polymer Interface

The nature of the filler-polymer interface has been the subject of many reviews, which dealt almost exclusively with aspects of bond strength in solids. The interaction between filler and molten polymer and their influence on rheological behavior have seldom been studied; however, some general comments can be made considering the differences between the boundary layers of particles suspended in low-molecular-weight and in high-polymer liquids. In the case of low-molecular-weight liquids, the interfacial layer is only several Angstroms (Å) thick, whereas, in high-molecular-weight fluids, it may reach several μ (20). The existence of this layer affects the rheological behavior of filled polymers. At low filler concentrations, the effective particle dimension is larger and the concentration dependence of, e.g., viscosity is steeper than that which could be predicted by common theories. At a higher concentration, a macromolecule may participate in boundary layers of several particles, leading to the formation of a "secondary quasi-crosslinked network," which shows time-dependent rheological behavior. Faitelson and Jakobson (21), working with 8 percent solution of polyisobutylene in cyclohexane filled with chalk (particle size, 1 to 2 μm), determined that secondary structures formed at volume fraction $\phi = 0.15$.

It is not known whether the existence of the relatively thick boundary layer in filled melts is a general phenomenon. It may be noted that, in some cases, preferential adsorption of polymers (viz., PS on mica) has been observed (22). It has been reported that an adsorbed macromolecule assumes a random coil configuration (22, 23) although, as De Gennes (8) discussed, this problem is far from settled.

One additional observation may be important—that of a preferential adsorption of polymeric macromolecules on specific sides, or planes, of a filler. In particular, for minerals with preferential cleavage planes, the physical attachment of macromolecules to these will be less likely than to other, less regular, planes. In the case of mica flakes, such a preference may increase the apparent aspect ratio, as well as the effect of the filler, on the rheological behavior of the melt.

Filler-Filler Interactions

The particles of a finely divided solid are held together by a variety of forces: Van der Waals, electrostatic, liquid bridges, etc. (24). In general, the filler-filler bonds are stronger than the matrix-filler ones (25). As a consequence, the particles resist dispersion and tend to aggregate. In case of the small particulate fillers, such as carbon black or fumed silica, three dimensional structures may form throughout the melt. The presence of aggregates is undesirable, since it has negative effects on mechanical properties of the composite. The rheological properties of filled melts are further affected by the presence of aggregates. An aggregate can be considered to be a large particle with its

Table 3. Particle Dimensions and Shapes of Typical Fillers

Filler	Density ρ(g/ml)	Hardness (Mohs)	Typical Particle Size (μm)	Particle shape	Refs
Alumina trihydrate (ATH)	2.4	2.5	2-20	irregular	12
Calcium carbonate	2.71	3	1-10	irregular	13
Talc	2.4	1	3-8	platelets aspect ratio 5.1 to 10.1	14
Mica	2.83	2-3	thickness $t \geq 1$	thin platelets 10-80 (μm) size	15
Wollastonite	2.98	4.5	10-30 aspect ratio 3.1 to 20.1	acicular	16
Glass fiber	2.55	6	diameter 9 to 18	fiber	17
Glass beads	2.5	6	30	spherical	17
Glass microballoons	0.1-0.5		70	spherical	18
Silica	2.6	7	Natural 2-12 synthetic 0.01-01.	complex spherical	19

interstitial spaces filled with immobilized polymer; i.e., the system behaves as if the filler concentration were actually higher than that which has been added.

The best-known method to improve filler dispersion involves a treatment with compounds (26) that reduce the filler-filler interactions and at the same time improve the filler-polymer bonding. (viz. Table 4) These surface-active agents, called sizing or coupling agents, are also known to affect the machine wear (27).

It has been reported (28, 29) that, for some polymer melts containing filler treated with a coupling agent, the flow curve (shear viscosity, η, *vs.* rate of shear, $\dot{\gamma}$) may cross over and fall below that of the pure polymer. Such a reduction of η, related to the change of the flow mechanism, may be of great practical significance.

RHEOLOGY OF NEWTONIAN LIQUID SUSPENSIONS

Zero Shear Properties

The theoretical calculations for the zero shear viscosity of suspensions have been based on hydrodynamics (30, 31). These considerations invariably lead to a power series type of equations for relative viscosity:

$$\eta_r = \eta/\eta_0 = \sum_{i=0}^{n} a_i \phi^i \qquad (1)$$

where η and η_0 are the zero shear viscosities of suspension and the suspending medium, respectively, and ϕ is the volume fraction of suspended particles. The classical Einstein solution (32) for infinitely dilute hard-sphere suspensions gives:

$$a_o = 1, \qquad a_1 = 5/2, \qquad a_i (i \geq 2) = 0.$$

Simha (33) extended this treatment to rigid dumbells, where:

$$a_1 = 3(L/a)^2/2$$

(L is the sphere's separation and a their diameter), and (34a) to ellipsoids of rotation and rigid rods:

$$a_1 = \frac{14}{15} + \frac{p^2}{5}\left(\frac{1}{3(\ln 2p - \lambda)} + \frac{1}{\ln 2p - \lambda + 1}\right) \qquad (2)$$

Table 4. Effect of Filler Treatment (26). Percent of Viscosity Change of Filled Mineral Oil; Brookfield Viscometer; $\dot{\gamma} = 1$

0.4% additive based on filler	Suspensions Containing: 27% Silica	50% $Al(OH_3)$	50% $CaCO_3$
	ORGANIC ADDITIVES		
Control (cp)	25,000	22,100	40,500
Undecenoic acid	−35	−93	−93
1-Decanol	−38	−48	−49
1-methoxy-2 propanol	−40	−52	−53
Hexylamine	−68	−56	−54
$Ti(OBu)_4$	−69	−95	−95
$Al(OBu)_3$	−62	−85	−69
	SILANE ADDITIVES		
Z-6030	−52	−86	−47
Z-6030W decanol	−56	−85	−70
Z-6030—$Ti(OBu)_4$	−64	−92	−91
Z-6030—$Al(OBu)_3$	−64	−88	−80
Z-6032z (S) (Dow PM)	−43	−72	−70
Z-6032 (Dow PM)	−49	−84	−75

where $p = b_1/b_2$ is the aspect ratio, with b_1 and b_2 being the major and minor axes of rotation, respectively, and λ a numerical constant. For ellipsoids of rotation, $\lambda = 1.5$, and for rigid rods, $\lambda = 1.8$. *Equation 2* holds for $p > 20$; for lower aspect ratios, see Ref. 34b and the references listed there.

As the concentration increases, so does the need for higher terms in *Eq 1*. However, even for moderate concentrations, the theoretical difficulties become very severe, indeed; the values $a_2 = 2.5$ to 14.1 have been reported by different authors (39). A significant breakthrough has been published by Simha in 1952 (35). The author used a cell model of the hard sphere suspension, placing the particles in the center of the spherical shells, with radius, inversely proportional to ϕ, dependent on the hydrodynamic interactions. The rigorous treatment of the model resulted in the closed form relation:

$$\eta_r = 1 + 2.5\lambda\phi$$
$$\lambda = 4(1 - Y^7)/(4(1 + Y^{10}) - 25Y^3(1 + Y^4) + 42Y^5)$$
$$Y = (2(\phi_m/\phi)^{1/3} - 1)^{-1} \qquad (3)$$

It can be seen that *Eq 3* for $\phi \to 0$ reduces to Einstein's solution, and for $\phi \to \phi_m$, $\eta_r \to \infty$, as it should.

There are many $\eta_r = \eta_r(\phi)$ relations in the literature (36-38). Among them, the more successful or more recent are:

Krieger (39) $\eta_r = (1 - K\phi)^{-a_1/K}$ (4)

Fedors (40) $\eta_r = [1 + 1.25\phi/(\phi_m - \phi)]^2$ (5)

Quemada (41) $\eta_r = (1 - \tilde{\phi})^{-2}$; $\tilde{\phi} = \phi/\phi_m$ (6)

Gillespie (42) $\eta_r = (1 + \phi_{eff}/2)/(1 - \phi_{eff})^2$ (7)

where:

$$\phi_{eff} = \phi + k\phi^2;\ k = (1 - \phi_m)\phi^{-2}.$$

It can be seen, that *Eq 6* can be considered as a specific case of *Eq 4* with $a_1 = 2K = 2/\phi_m$. Since for $\phi \to 0$ it is expected that $a_1 \to 2.5$, then $K = 1.25$ and ϕ_m in *Eq 6* equals 0.8. *Equation 4*, written as:

$$\eta_r = (1 - \tilde{\phi})^{-2.5} \qquad (4a)$$

has been used (45) as a semiempirical formula to describe the viscosity-concentration dependencies of suspensions containing particles of different shapes and sizes; in these cases, ϕ_m was determined by centrifugation. The relations *Eqs 6* and *7* are relatively recent and need detailed examinations.

On the basis of the free-volume theory of liquids, Utracki (44, 45) derived the following dependence for the solution viscosity:

$$\ln \eta_r = D_0 + D_1/(1 + D_2\phi) \qquad (8)$$

where D_i are parameters of the equation. For single-structure liquids:

$$D_0 = -D_1$$

Furthermore, the temperature dependence of η_r is through D_2 only:

$$D_2 = h \exp\{0.11515[(T/T_{g,1})^{3/2} - (T/T_{g,2})^{3/2}]\} - 1 \quad (9)$$

where h is a hydrodynamic shielding parameter and $T_{g,i}$, $i = 1,2$ are the glass transition temperatures of the dispersed and continuous phases, respectively. For hard-sphere suspensions, $a = 5/2$, and *Eq 8* can be written as:

$$\ln \eta_r = 2.5\phi/(1 + D_2\phi) \quad (8a)$$

or in a linear form:

$$1/\ln \eta_r = (1/D_0) + (1/D_0D_2)(1/\phi). \quad (8b)$$

Equation 8a is the Mooney (46) equation with an adjustable parameter D_2.

The relative merit of these relations can be evaluated by comparison with the Thomas empirical dependence (42).

$$\eta_r = 1 + 2.5\phi + 10.05\phi^2 + 0.00273 \exp\{16.6\phi\} \quad (10)$$

(note that $\eta_r \to 44{,}216$ for $\phi \to 1.0$!). This equation was fitted to viscosity data of suspensions of uniform spherical particles obtained in sixteen different laboratories. The particle diameters varied from 0.099 to 435 μm. Both aqueous and nonaqueous systems were measured with $0.0 \leq \phi \leq 0.7$ (see *Fig. 1*). By appropriate extrapolation methods, Thomas minimized the spread of data (due to non-Newtonian, inertial, and nonhomogenous suspension effects) and obtained a generalized dependence, shown in *Fig. 2*. *Equation 10* represents this generalized behavior. The experimental spread of the corrected η_r in *Fig. 2* is ± 13 percent at $\phi = 0.5$.

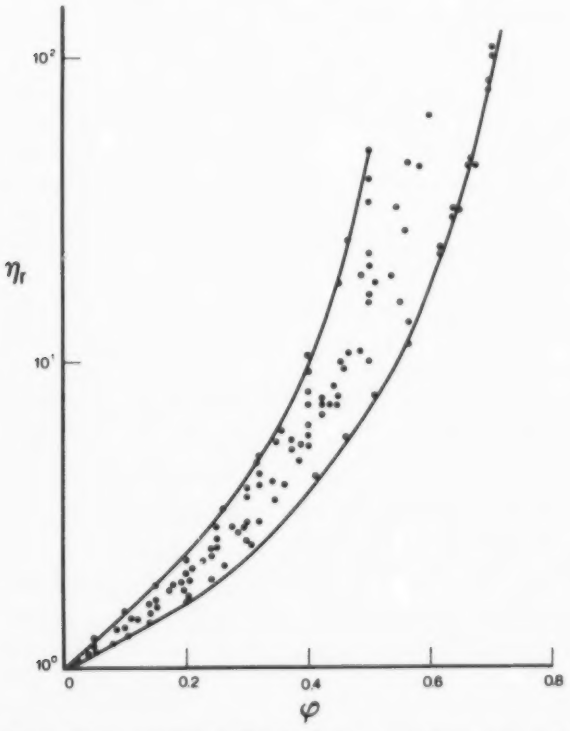

Fig. 1. Relative viscosity of hard spheres suspensions, η_r vs. volume fraction, ϕ. Raw data (47).

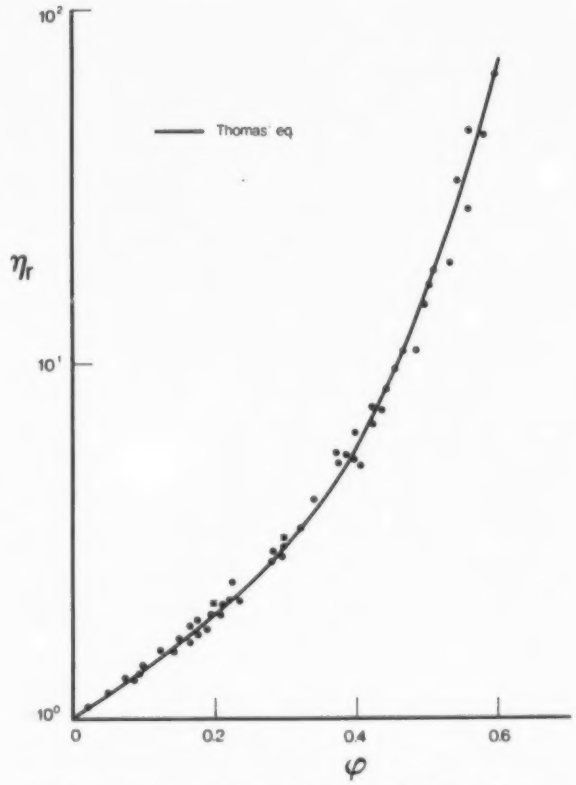

Fig. 2. Corrected η_r vs. ϕ of hard spheres (47). The solid line represents Eq 10.

In order to evaluate the *Eqs 3* to *8a*, the numerical values of η_r were computed from *Eq 10*. Setting $a_1 = 2.5$, *Eqs 3* to *8* were treated as single-parameter dependencies. The value of this parameter was calculated by equating:

$$\eta_r(i) = \eta_r(10)|_{\phi=0.5}$$

(here the values in parenthesis refer to equation number: $i = 3, 4 \ldots 8a$). Next, for $\phi < 0.65$, the values of η_r and the deviation:

$$\Delta\eta_r = 100[1 - \eta_r(i)/\eta_r(10)] \quad (11)$$

were computed. The values of $\Delta\eta_r$ are shown in *Fig. 3* and *Table 5*. It should be noted that *Eq 10* is valid only within the experimental range of data used to define it; i.e., $\phi \leq 0.6$. The dependence does not predict $\eta_r \to \infty$ at any realistic concentration $\phi \leq 1.0$. For this reason, the average, absolute deviation, $|\overline{\Delta\eta_r}|$, and the absolute maximum deviation, $|\Delta\eta_{r,max}|$ quoted in *Table 4* were computed for $0 \leq \phi \leq 0.6$ only.

On the basis of the results presented in *Fig. 3* and *Table 5*, it is apparent that the experimental data (as represented by *Eq 10*) follow the theoretical equations in the following order of accuracy: *Eq 8a*, *Eq 3*, *Eq 7*, and *Eq 6*. Since the remaining dependencies deviate more than the experimental spread of data; i.e., here $|\Delta\eta_{r,max}| > 13$, they will not be discussed. In *Fig. 4*, the values calculated from the four best equations (points) are compared with the experimental curve (solid line) defined by *Eq 10*.

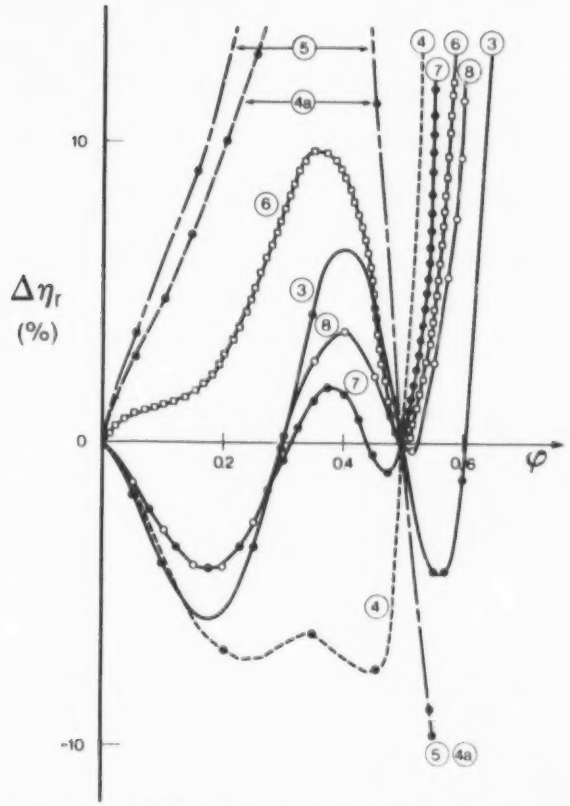

Fig. 3. Percent of difference between the theoretically predicted and empirically determined η_r as a function of ϕ. Numbers refer to the equations as listed in the text.

A short note regarding *Eq 8b*. *Figure 5* illustrates the linearization of the data discussed above. Relaxing the hard sphere requirement that $D_0D_2 = a_1 = 2.5$, one can use this type of plot to generalize any η_r *vs.* ϕ dependence, provided that the structure of liquid does not change within the range of the experimental conditions (44, 45).

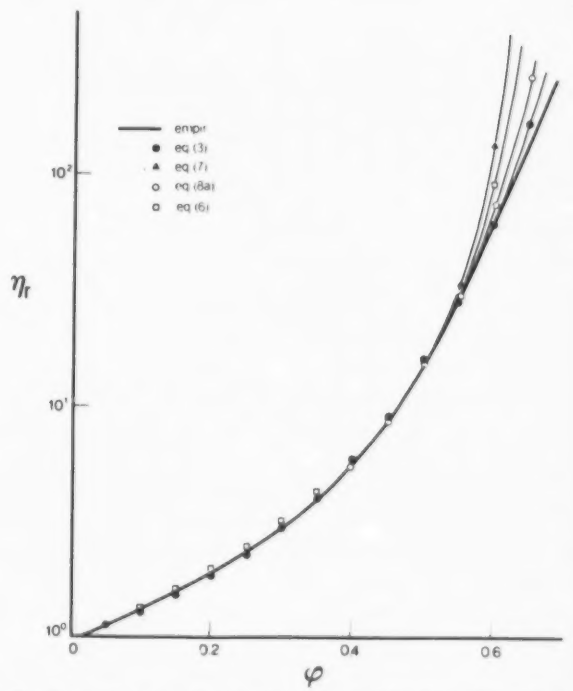

Fig. 4. η_r vs. ϕ, as given by the empirical Eq 10 and predicted theoretically by Eqs 3, 6, 7, and 8a. The parameters of these equations are listed in Table 4.

Earlier, *Eq 3* had been successfully used (48) for hard sphere suspensions of PVC latexes and organosols. In these cases, ϕ_m was determined by centrifugation in a similar manner, as described in relation to application of *Eqs 4a* and *5*.

There are three aspects that may significantly complicate the analysis of η_r *vs.* ϕ dependence:

- polydispersitv
- particle shape
- structure formation

The polydispersity aspect was discussed by Farris (49) and Parkinson, *et al.* (50). The overall relative vis-

Table 5. The Deviation, $\Delta\eta_r$, computed from Eq 11 for Eqs 3 to 8a

ϕ	Eq 3	Eq 4	Eq 5	$\Delta\eta_r$(%) Eq 6	Eq 7	Eq 4a	Eq 8a
0.00	0	0	0	0	0	0	0
0.05	−1.683	−1.459	3.165	1.025	−1.257	2.793	−1.299
0.10	−3.991	−3.652	6.340	1.314	−2.872	4.863	−2.991
0.15	−5.590	−5.691	8.985	1.733	−3.998	7.044	−4.162
0.20	−5.559	−6.917	12.217	2.967	−4.000	10.009	−4.108
0.25	−3.551	−7.154	16.123	5.175	−2.725	13.864	−2.600
0.30	0.123	−6.721	19.973	7.859	−0.576	17.912	0.028
0.35	4.207	−6.420	21.966	9.693	1.366	20.377	2.706
0.40	6.465	−7.044	19.584	8.845	1.644	18.681	3.779
0.45	4.887	−7.511	11.490	4.623	0.034	11.258	2.273
0.50	0.005	−0.006	0.004	0.000	−0.000	0.001	0.001
0.55	−4.233	64.602	−8.842	4.063	14.675	−9.775	2.709
0.60	−1.224		−5.161	49.299	117.313	−10.704	22.341
0.65	22.681		49.174	842.856		14.267	274.148
Parameter:							
	ϕ_m = 0.7864	K = 1.6896	ϕ_m = 0.71055	ϕ_m = 0.66844	ϕ_m = 0.65021	ϕ_m = 0.74848	D_2 = 1.09312
$\overline{\lvert\Delta\eta_r\rvert}$	3.66	10.651	11.74	4.30	3.01	10.60	2.42
$\pm\sigma$	2.17	18.07	7.09	3.31	4.12	6.67	1.45
$\lvert\Delta\eta_{r,max}\rvert$	6.465	64.602	21.996	9.693	14.675	17.912	4.162

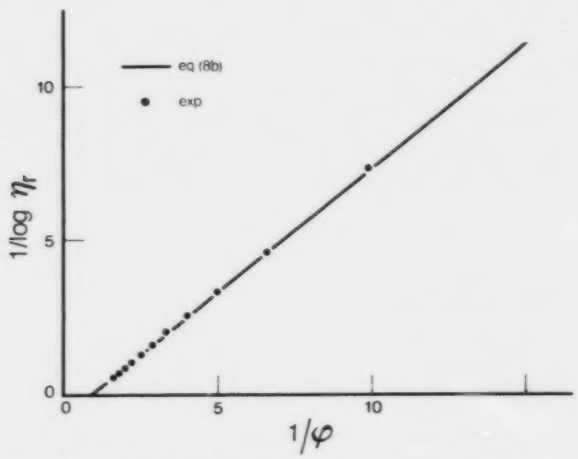

Fig. 5. Linearization of η_r vs. ϕ dependence according to Eq 8b. Points: experimental data.

cosity of polydisperse suspension can be calculated as (49):

$$\eta_r = \prod_i \eta_{r,i}(\Phi_i);\ \Phi_i = V_i/\sum_i V_i \qquad (12)$$

and V_i is the volume of the ith generation of spheres. It is customary to assign the subscript $i = 0$ to the liquid and $i = 1$ to either the smallest or the largest particles. *Equation 12* shows that, in order to operate at a minimum value for η_r at a constant-total-solids volume-fraction, ϕ_T, the distribution of the discrete particles should be:

$$\Phi_i = \text{const.}$$

Note that Φ_i in *Eq 12* is defined, *not* in the customary way as a volume fraction of the *total*, but as a volume fraction of the volume up-to-and-including the ith generation of spheres!

In the second publication on the subject (50), the viscosity of disperse spheres suspension is written as:

$$\eta_r = \prod_i \exp\{2.5\ \phi_i/(1 - k_i\phi_i)\} \qquad (13)$$

where ϕ_is are the volume fractions of each generation of (spherical) particles and k_is depend on the particle diameter D_i^* according to the empirical relation:

$$k_i = 1.079 + \exp\{0.01008/D_i\} + \exp\{0.00290/D_i^2\}$$

The effect of bimodality of particle distribution is demonstrated in *Fig. 6* (50). The minimum in the experimental dependence is a result of the increase of packing efficiency; i.e., increase of ϕ_m, due to blending particles of different diameters. A large body of literature on the subject accumulated over the years. White and Walton (51) calculated that, by selecting generations of spherical particles of proper relative diameters and composition, one can increase ϕ_m from 0.7404 (single generation) to: 0.793 (binary), 0.810 (tertiary), 0.842 (quaternary), 0.851 (quinary), and 0.961 (hexagenary). Similar calculations (48) were qualitatively confirmed by blending specially prepared PVC latexes and subsequently measuring the η_r *vs.* ϕ dependence. The difference between the computation and experiments stems from the initial assumption of a perfect hexagonal

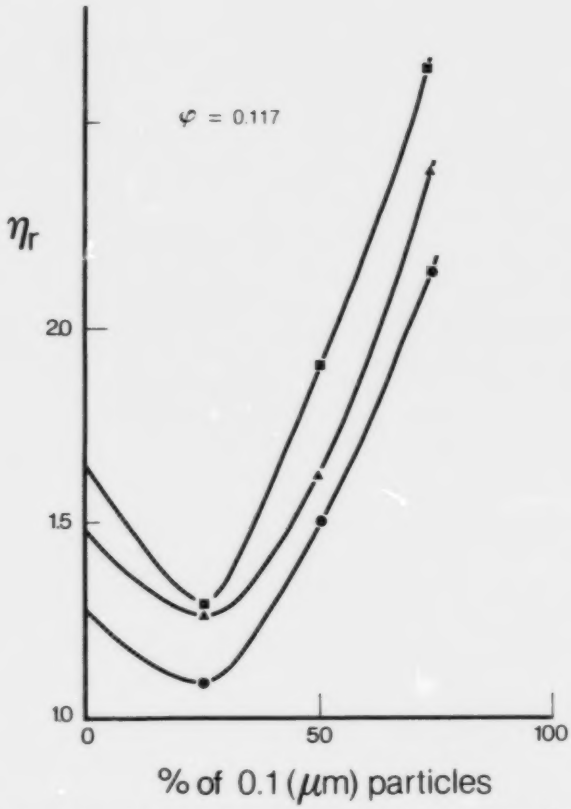

Fig. 6. Effect of composition of suspension in bimodal size distribution of η_r, $\phi = 0.117$; squares = 0.6, triangles = 1, circles = 4 (μm) diameter particles added to 0.1 (μm) ones (50).

packing with the coordination number of $N^c = 12$. The values of ϕ_m for mono- and multimodal suspensions are listed in *Table 6*.

For nonspherical particles of length-to-diameter (or aspect) ratio, p, the parameter $\phi_m = \phi_m(p)$. *Figure 7* illustrates the experimental dependence (59) where the ϕ_m^d refers to the dry packing; note that, for p increasing

Table 6. Packing Efficiency (51-58)

N°	Suspension of		ϕ_m
I	Spheres: monomodal	N^c	
	hexagonal	12	0.7404
	face-centered cubic	12	0.7404
	body-centered cubic	8	0.60
	cubic	6	0.52
	random (theoretical)	—	0.637
	random (experimental)	—	0.60-0.64
II	Spheres: bimodal		
	random,		
	$d_2/d_1 = 1$		0.636
	$d_2/d_1 = 3.8$		0.684
	$d_2/d_1 = 47$		0.814
	$d_2/d_1 =$		0.868
III	Spheres: quatromodal		
	theory		0.98
	experiment		0.81
IV	Crushed glass rod particles		
	monomodal		0.476-0.500
	bimodal		0.566
V	Precipitated $CaCO_3$		0.36-0.50
VI	Aluminium powder		0.25-0.32

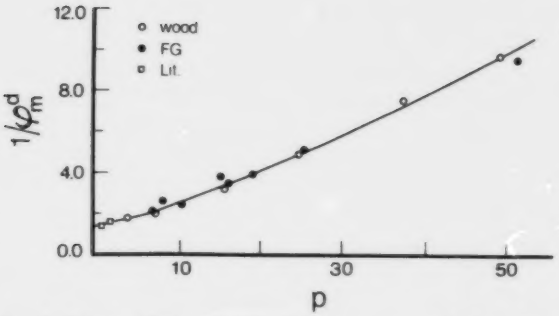

Fig. 7. Effect of rod aspect ratio, p, on maximum dry-packing volume fraction (59).

from 1 to 50, ϕ_m^d decreases from 0.63 to 0.11. In particular, for $p = 38$, the dry packing $\phi_m^d = 0.14$; furthermore, it is worth comparing this value with $\phi_m = 0.31$, calculated from η of suspension of rods with $p = 38$, by Fedors (40). There are few possible reasons for the disagreement: the difference in polydispersity, reduced friction coefficient in suspension, nonrandom orientation of rods in a flowing system, and partial attrition on handling.

The above discussion on ϕ_m for rods is also applicable to discs (flakes); for random loading, ϕ_m decreases with p (defined here as diameter-to-thickness ratio), ϕ_m^d for dry packing is lower than that calculated from solution, etc. As Mason (60) demonstrated, both discs and rods show a similar behavior in flow—above certain critical concentration, ϕ_c, their rotation is impossible, and a plug flow is obtained. In general, $\phi_r \leq \phi_m^d \leq \phi_m$.

The second source of difference between hard sphere and nonspherical particle suspensions is the value of the intrinsic viscosity, a_1. As demonstrated above, for spheres, $a_1 = 5/2$ is well established theoretically and verified by experiments. For suspensions or ellipsoids and rods, a_1, calculated from *Eq 2*, is shown in *Table 7*.

The rheology of disc suspensions was studied by Lingard and Whitmore (61). Their experimental results of a_1 *vs.* p are shown in *Fig. 8*. The value $a_1 = 8.52$, calculated from the empirical equation (61):

$$\ln \eta_r = 8.52\, \phi, \qquad (14)$$

derived from glass fiber ($p = 37.8$) suspension, is also shown. It can be seen that the experimental values are significantly lower than those predicted by *Eq 2*. Mason, *et al.* (60), have demonstrated that a_1 is sensitive to particle orientation. For time average optimum orientation, one can write

$$a_1 = p^3/[3(\ln 2p - \lambda)(p + 1)^2] \qquad (2a)$$

Table 7. Intrinsic Viscosity of Nonspherical Particles

p	A_1 (ellipsoids)		a_1 (rods)	
	Eq 2	Eq 2a	Eq 2	Eq 2a
5	(4.71)	1.442	(5.81)	2.303
10	(8.04)	1.842	(13.63)	2.304
20	38.203	2.763	42.743	3.201
40	120.375	4.403	131.579	4.915

Note: The values in parentheses are taken from (34b)

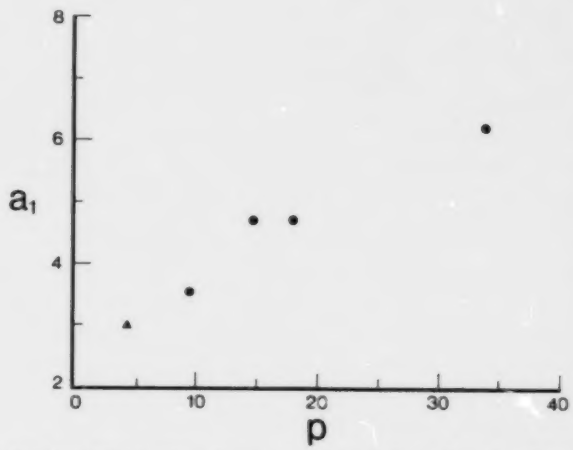

Fig. 8. Intrinsic viscosity, a_1 vs. aspect ratio, p, for discs (circles), red cells (triangle) (61), and glass fibers (square) (61).

The values of a_1 from *Eq 2a* form a lower limit for this parameter (see *Table 7*). The experimental values of *Fig. 8* are inside the bounds defined by *Eqs 2* and *2a*.

The zero shear viscosity of suspensions also depends on the structure. In all of the above considerations, a uniformly dispersed system was assumed, but this assumption is rarely confirmed by experiments. In fact, in most cases, one form of a structure or another is obtained. Two types should be distinguished, (a) formed by the shear field (e.g., skin-core structures in long tube flows), and (b) formed by particle-particle interpenetration. The knowledge of structures (a) is important for proper interpretation of the flow phenomena, as influenced by the flow profiles (60,63-65) as well as of the shear coagulation (66). The knowledge of structures (b) is the key for utilization of suspension rheology in processing (37). Since the effective volume fraction of dispersed particles increases with the increase of association, the η_r is strongly affected. In general, η_r of this type of suspension depends on the shear history.

Shear-Dependent Properties

Shearing the suspensions may lead to any of the following phenomena:

- yield stress
- thixotropy; i.e., decrease of η with time
- rheopexy, or anti-thixotropy
- dilatancy, or shear thickening
- pseudoplasticity, or shear thinning

or their combination. Since these phenomena are well-described in the textbooks and reviews on the subject (38, 67-76), only a brief selective summary will be given here.

The yield stress phenomenon is illustrated in *Fig. 9*. The data demonstrate the influence of processing on the rheological behavior of mineral/water paste at constant concentration of solids (77). It can be seen that the milling time influences both the yield stress, σ_y (intercept), and the apparent viscosity, η_a (slope). *Figure 10* shows the concentration dependence of σ_y. The dependence can be approximated by the relation (77):

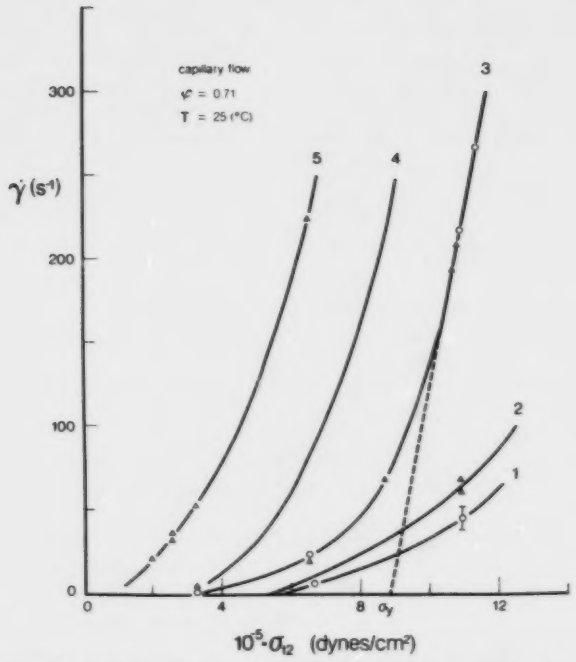

Fig. 9. Yield stress determination of mineral suspension in water at $\phi = 0.71$ and T = 25°C. Numbers refer to milling time in min just prior to the capillary flow measurements (77).

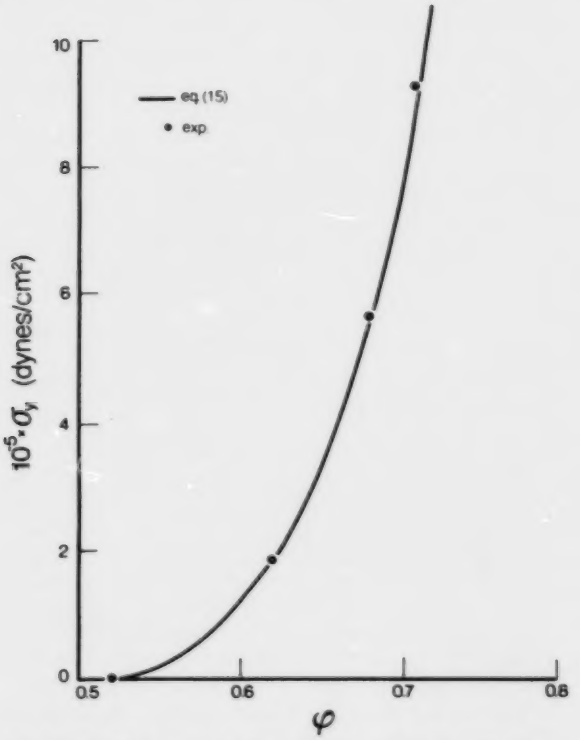

Fig. 10. Yield stress vs. ϕ for mineral suspensions. The curve represents Eq 15 dependence (77).

$$\sigma_y = K(\phi - \phi_0)^n \qquad (15)$$

where: ϕ_0 is the highest volume fraction of particles at which $\sigma_y(\phi) = 0$; K and n are parameters.

The effect of yield stress on the (uncorrected) flow curve $\eta = \eta(\phi)$ is shown in *Fig. 11*. Here, the suspensions of glass beads (ϕ indicated) in 4 percent solution of PIB in decaline was measured at 27°C in a rotational rheometer (78). The master curve was obtained by simultaneous vertical and horizontal shifts of raw data by η_0 and $\dot{\gamma}_0$, respectively. The concentration dependence of these parameters is shown in *Fig. 12*.

Both thixotropy and rheopexy are two faces of the same phenomenon: the relatively slow change of structure upon shearing. Rheopexy usually occurs in concentrated dispersions over a narrow range of $\dot{\gamma}$ beyond which only thixotropy is observed. This leads to discontinuity in flow curves (79), as illustrated in *Fig. 13*.

Thixotropy behavior may be described by the following relation (71).

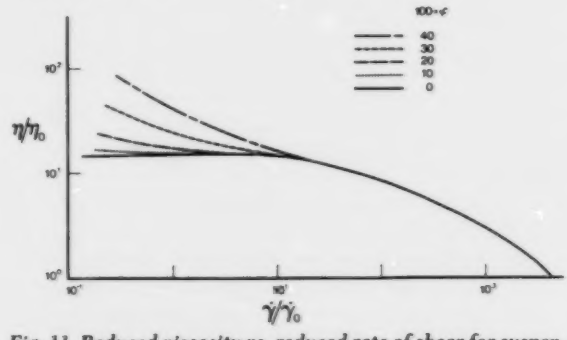

Fig. 11. Reduced viscosity vs. reduced rate of shear for suspensions of glass beads in 4% poly(isobutene) solutions in decalin ϕ = 0.0, 0.1, 0.2, 0.3, and 0.4, T = 27°C (78).

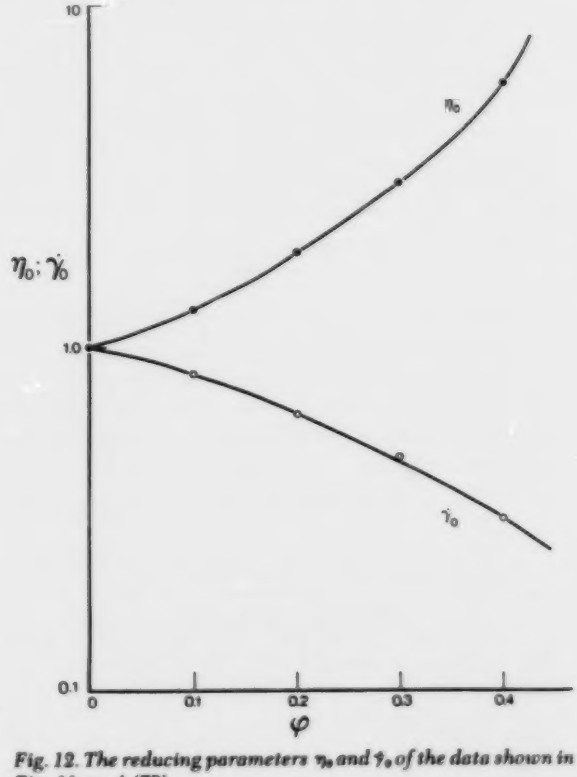

Fig. 12. The reducing parameters η_0 and $\dot{\gamma}_0$ of the data shown in Fig. 11 vs. ϕ (78).

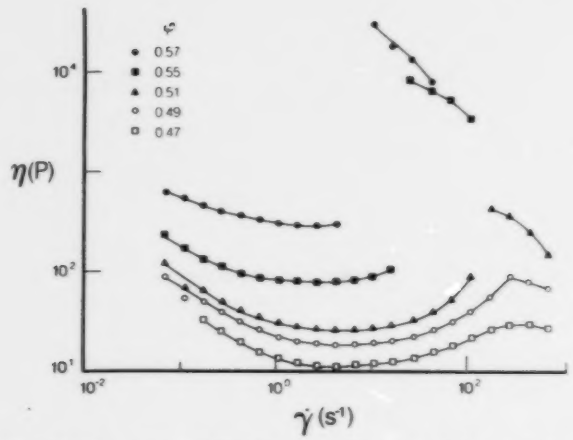

Fig. 13. Flow curves of PVC (particle diameter 1.25 μm) in dioctyl phthalate at 25°C for ϕ = 0.47, 0.49, 0.51, 0.55, and 0.57 (79).

$$\eta - \eta_\infty^t = (\eta_0^t - \eta_\infty^t) \exp\{-t/\tau^*\} \qquad (16)$$

where: η_0^t and η_∞^t refer to initial and final values of viscosity, t is the shearing time, and τ^* the relaxation time, dependent on ϕ, temperature, and $\dot{\gamma}$. Consequently, the flow curve of a dispersion may be given in terms of either η_0^t or η_∞^t, in the first case, the flow curve refers to the initial structure of the system whereas, in the second, to the continuously varying structure defined by the equilibrium morphology at a given $\dot{\gamma}$. The two flow curves can be taken as bounds for the apparent flow behavior. Unfortunately, authors frequently report η *vs.* $\dot{\gamma}$ curves without describing their data evaluation methods. These results are quite useless when time-dependent structures do occur. *Table 8* lists some examples of rheopectic systems.

Dilatancy and pseudoplasticity are both defined in terms of shear dependence of η—an increase and a decrease, respectively (80). Similar to rheopexy, the dilatancy is a less frequent phenomenon.

Two semi-empirical equations are used to describe the η *vs.* $\dot{\gamma}$ dependence for dispersions:
Cross (81):

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)/(1 + a\dot{\gamma}^b) \qquad (17)$$

and Krieger (82):

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)/(1 + \tau/\tau_a) \qquad (18)$$

In *Eq 17* η_0 and η_∞ correspond to η at $\dot{\gamma} = 0$ and $\dot{\gamma} \to \infty$, and a and b are constants. Cross introduced "a" as a ratio of kinetic constants, k_1 for link rupture and k_0 for the Brownian motion:

Table 8. Rheopectic Systems

No.	Medium	Dispersed phase Particles of	ϕ	d(μm)	References
1.	Plasticizers	PVC	0.26-0.55	0.05-0.7	85
2.	Water	Fe_2O_3	0.41-0	0.1-5.0	77, 86
3.	Water	SiO_2	0.62-0.87	2.5-25	87
4.	Plasma	blood cells	0.45-0.48	4.0	88
5.	Water	PS latex	0.4-0.5	0.1-0.6	89

$$a = k_1/k_0$$

Numerically, "a" can be considered as a measure of the characteristic rate of shear, $\dot{\gamma}_{ch}$, at which the value of $\eta = (\eta_0 + \eta_\infty)/2$; $\dot{\gamma}_{ch} = a^{-1/b}$. Values of a = 0.01 to 100 have been reported. The exponent "b" was originally thought to be b = ⅔, but later data indicated that its value varies with polydispersity (when applied to pseudoplastic polymer melts), and b ≅ 1 was frequently calculated. In *Fig. 14*, the usefulness of *Eq 17* is shown. The data (83) refer to the water-in-oil emulsion flow in rotational and capillary rheometers.

Equation 18 was derived from the consideration of the energy dissipation during doublet-formation of rotating spheres. Since

$$\eta\dot{\gamma} = \tau = \sigma_{12}, \qquad (19)$$

where τ is the true shear stress, the value of τ_a (which linearizes the dependence) is usually selected by trial and error.

Both *Eq 17*, with four adjustable constants, and *Eq 18*, with three, can be applied directly only to the systems without yield stress. One way to circumvent the problem of a yield stress is to incorporate the definition:

$$\sigma_{12} = \tau_0 - \tau_y \qquad (20)$$

(τ_0 and τ_y are, respectively, apparent and yield shear stress) into *Eqs 17* or *18*. The other is to write a constitutive equation. This latter approach yields a four-parameter "structure equation" (84):

$$\tau = \tau_y + \tau_0 + \eta_\infty\dot{\gamma} - \tau_0 \exp\{-a\dot{\gamma}\} \qquad (21)$$

(τ_y, τ_0, and a are parameters). *Equation 21* was recently evaluated and found successful for viscoelastic liquids, suspensions, and emulsions.

For a limited range of $\dot{\gamma}$, the "power law" equation

$$\eta = K_1\dot{\gamma}^{-m} \qquad (22)$$

(where: $K_1 = \eta(\dot{\gamma} = 1)$ and $0 \leq m \leq 1$ are constants) is most frequently used.

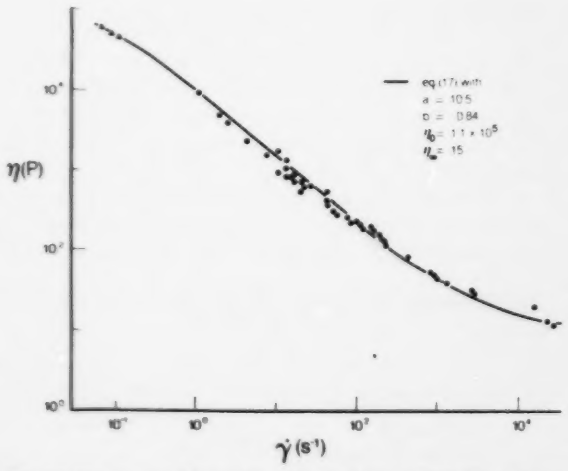

Fig. 14. Flow curve for water-oil emulsion at 25°C. Data from rotational and capillary rheometers; the curve represents the Cross Eq 17 with the parameters indicated (83).

The normal stress behavior was analyzed for dilute suspensions only. For the hard spheres, the first normal stress difference was expressed (90) as:

$$N_1 = \sigma \phi A(0.35 R_e^{0.5} - 3/4) \quad (23)$$

where σ is shear stress of medium and Re is the particle shear Reynolds number. For nonspherical particles (62):

$$N_1 = k\sigma\phi\dot{\gamma}\epsilon^2 D/[\dot{\gamma}^2 + 36D^2] \quad (24)$$

where k is a constant, ϵ is a measure of deviation from sphericity, and D is the rotational Brownian diffusion coefficient. Both *Eqs 23* and *24* are valid for suspensions in Newtonian liquids. The inertial effect of particles causes $N_1 < 0$ for low values of Re (viz., *Eq 23*). For small D (i.e., for large particles), *Eq 24* predicts that N_1 is independent of $\dot{\gamma}$ but varies with ϕ and ϵ^2.

The elongational viscosity, η_e, of suspensions strongly depends on the aspect ratio (92-94). As indicated in the last column of *Table 9*, the ratio η_e/η for rodlike suspensions is about eight times larger than predicted by the Trouton rule and as observed for pure liquids. It was reported (93) that, for glass fiber dispersed in polybutene ($\rho = 0.89$ g/cm^3; $\eta = 283$ (*P*)), $T = 23$°C η_e follows the theoretical dependence:

$$\eta_e/\eta = 3 + 4\ \phi p^2/3\ \ln(\pi/\phi)$$

the p varying from 282 to 1259 and $\phi = 0.01$.

RHEOLOGY OF FILLED POLYMER MELTS

From the point of view of rheology, the filled polymer melts can be treated as a particular class of suspensions in which the suspending medium is a viscoelastic liquid. This means that, in addition to all the effects caused by addition of particulates into a Newtonian liquid (discussed in the previous section), one has to add the effects introduced by the viscoelastic and macromolecular character of the dispersing medium. Investigation of the entirety of this complex problem began only recently.

Most of the studies have been done at a single, high rate of shear in capillary rheometers (95-101). The first study in which a wide range of $\dot{\gamma}$ was covered is dated 1969. The authors (102) showed that talc-filled PP at low $\dot{\gamma}$s exhibited a strong yielding. Within the higher range of $\dot{\gamma} > 1$, the flow curves (see *Fig. 15*) for $\phi \leq 0.2$ follow a single dependence. The σ_y, as expected, was found to change with the filler surface treatment. Similar effects were reported (103) for PP/short-glass-fiber systems (shown in *Fig. 16*), for glass-bead-filled styrene acrylonitrile (SAN) copolymer (104) and others.

Table 9. η and η_e for Suspension of Glass Fibers, $\phi = 0.013$, p = 57 (92)

No.	Fluid	η(P)	η_e(P)	η_e/η
1.	Newtonian liquids			
	Silicone oil	1,000	3,000	3
	Indopol (polybutene oil)	205	615	3
2.	Suspensions			
	in silicone oil	1,150	29,000	25
	in Indopol	235	5,400	23

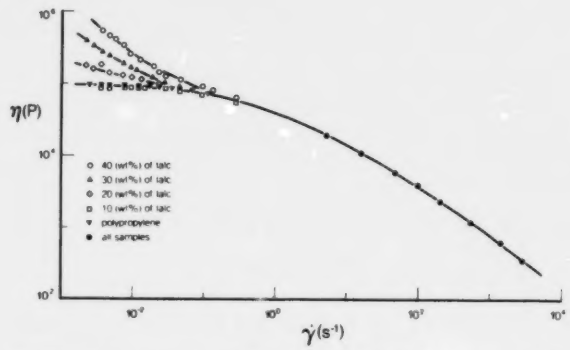

Fig. 15. Flow curves from PP at 200°C filled with 0.0, 10, 20, 30, and 40 wt.% of talc (102).

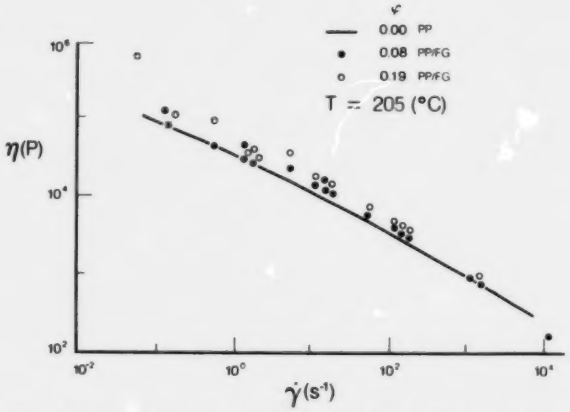

Fig. 16. Flow curves for PP at 205°C filled with $\phi = 0.0, 0.8$, and 0.19 of glass fibers (103).

In the first report on the flow behavior of polymer (PP) filled with mica flakes by Okuno and Woodhams (105), a very steep increase of η with an increase of ϕ was observed (see *Fig. 17*). This effect is particularly strong at low $\dot{\gamma}$s, suggesting the yield phenomenon.

During the past few years, filled polymers have become one of the most interesting systems for rheological studies (95-126). The notable publications on the subject are summarized in *Table 10*. Here, under the heading "Measurements," the first two columns indicate the maximum volume fraction of the particulates, ϕ_{max}, and the minimum value of the rate of shear (s^{-1}) or frequency in (rad/s), $\dot{\gamma}_{min}$ used in the measurements. The remaining four columns indicate which rheological property was measured or observed: η = shear viscosity, N_1 = normal stress difference, σ_y = yield stress, and η_e = elongational viscosity.

From the data in *Table 10*, one can see that (excluding elastomers) the most investigated filled polymer is PP, then PE and PS, followed by the others. Most of the data are obtained in shear flow without measuring the N_1. η_e was determined for a few systems only.

Shear Viscosity

Three phenomena should be considered:

(1) σ_y = yield, (2) $\eta = \eta(\phi)$, and (3) the η-anomaly.

(1) For the proper understanding of flow, yield effects

Table 10. Summary of Melt Rheological Investigation of the Composites

No.	Polymer/filler	Particulates d(μm)	Particulates p	ϕ_{max}	$\dot{\gamma}_{min}$	η	Measurements N_1	Measurements σ_y	Measurements η_e	Ref.
I	POLYETHYLENE (PE)									
1.	Fiber glass (FG)	10	400	0.20	30	η	—	Y	—	106
2.	Chalk, limestone	15	—	0.45	10	η	—	—	—	107
3.	FG	—	—	0.19	0.002	η	—	?	Y	108
4.	TiO_2	—	—	0.36	0.008	η	B	Y	—	109
5.	FG	12.7	157	0.19	0.005	η	Y	Y	Y	110
6.	Glass Balloons (GB)	53	—	0.653	10^{-9}	η	—	Y	—	111
	Carbon Fibers (CF)	10	60	0.044	10^{-3}	η	—	N	—	111
7.	FG	725	35	0.09	100	η	—	N	—	112
8.	Mica	—	—	0.33	0.01	η, η^*	G′	—	—	this work
II	POLYSTYRENE (PS)									
1.	Glass powders	0.02	0 to	0.08	0.8	η	—	Anomaly	—	113
	Kaolin, Alumina. . .	to	20							
		180								
2.	FG	12.7	15	0.22	0.01	η	Y	N	—	114
	Aramid (Kevlar)	12.2	60	0.18	0.01	η	Y	N	—	114
	Cellulose	12	100	0.20	0.01	η	Y	N	—	114
3.	$CaCO_3$	0.5	—	0.2	0.01	η	Y	Y	Y	115
	Carbon black (CB)	0.045	—	0.2	0.01	η	Y	Y	Y	115
	TiO_2	0.18	—	0.2	0.01	η	Y	Y	Y	115
	Franklin Fiber	1.5-2	100	0.2	0.01	η	Y	Y	—	115
	Mica	5	25-50	0.2	0.01	η	Y	N	—	115
	Glass Beads	10	—	0.2	0.01	η	Y	N	—	115
4.	Glass Beads	36	—	0.369	10^{-3}	η	—	Y	—	111
5.	FG	12.7	157	0.2	10^{-3}	η	Y	N	Y	110
6.	$CaCO_3$	0.5	—	—	—	η	Y	Y	Y	116
	CB	0.045	—	—	—	η	Y	Y	Y	116
III	POLYPROPYLENE (PP)									
1.	Talc	10	—	0.2	10^{-3}	η	—	Y	—	102
	Glass Beads	44	—	0.2	10^{-3}	η	—	Y	—	102
2.	FG	—	—	0.2	0.38	η	—	N	—	117
3.	FG	—	—	0.194	0.1	η	—	?	—	103
4.	Mica	6.7	65	0.15	2.5	η	—	?	—	105
5.	$CaCO_3$	—	—	—	—	—	—	—	—	118
6.	Fluoroplast	1.0	?	0.01	—	η	—	Anomaly	—	113
7.	FG	725	35	0.09	100	η	—	N	—	112
8.	Talc	30	—	0.2	150	η	B, Bagley	N	—	119
9.	FG (B)	10	50	0.07	3	η	B, Bagley	N	—	120-121
	FG (C)	10	30	0.11	1	η	B	N	—	121
	FG (D)	10	500	0.09	1	η	B	N	—	121
	FG (E)	10	1000	0.09	1	η	B	N	—	121
	FG (F)	10	2000	0.09	1	η	B	N	—	121
10.	FG	10	300	0.11	10	η	—	N	—	122
11.	Mica	—	—	0.17	0.5	η	—	N	—	29
	$CaCO_3$	—	—	0.22	0.2	η	—	N	—	29
IV	POLYVINYL CHLORIDE (PVC)									
1.	$CaCO_3$	?	—	0.21	?	η	—	—	—	123
	Mica	6	62.4	0.21	?	η	—	—	—	123
V	POLYCARBONATE (PC)									
	FG	12	?	0.24	0.1	η	Y, B	Y	—	124
VI	POLYAMIDE 6 (PA-6)									
	FG	10	300	0.11	10	η	—	—	—	122
VII	POLYAMIDE 6,6 (PA-6,6)									
	FG	10	30	0.19	10	η	B	N	—	121
VIII	RUBBERS									
	A. SBR/CB	0.045	—	—	—	—	—	?	—	98
	B. NR/CB	0.17	—	0.5	4.5	η	B	?	—	125
IX	SURLYN IONOMER									
	Perlite	5.5	—	0.15	0.04	η	Y	Y	—	126
X	POLY(STYRENE-CO-ACRYLONITRILE) (SAN)									
	Glass Beads	—	—	—	—	η	—	N	—	102

Notes: Significance of the symbols used in Table 10: η, η^* = steady state and dynamic viscosities, respectively; " – " = not measured, Y = yes; N = no; B, G′, and Bagley = methods of measurements of the normal stress via: die swell, storage modulus, and from Bagley correction, respectively; "Anomaly" = rapid decrease of with addition of small volume of particulates: ? = uncertain.

may be separated by standard methods of data treatment, viz., *Fig. 9*. Dependencies, such as those shown in *Figs. 15* to *17*, indicate yielding. It is obvious that this is a general phenomenon in filled-polymer melts, favored by a decrease of particle size (127), an increase of ϕ, and a decrease of $\dot{\gamma}$. Plot of σ_y *vs.* ϕ (111) is shown in *Fig. 18*. Modification of particle surface changes σ_y (114, 124, 126).

(2) As shown in *Fig. 15*, for PP/talc above a certain value of $\dot{\gamma}$, the viscosity η for all compositions follows the same curve. Similar results were reported by Goel (119)

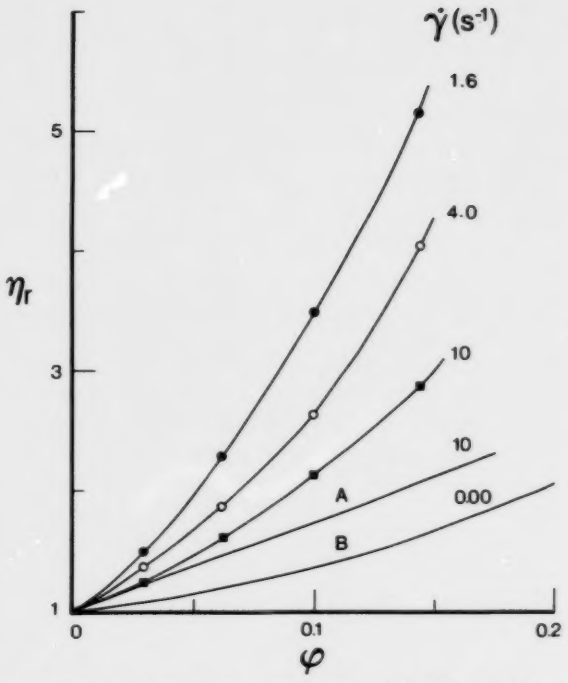

Fig. 17. Relative viscosity at constant $\dot{\gamma}$ vs. ϕ for PP/mica (three upper curves), for PP/$CaCO_3$ ($\dot{\gamma}$ = 10), and as calculated from Eq 2; i.e., at $\dot{\gamma}$ = 0 (105) (see text).

for the same system, and for PP/FG by Charrier (103) (see *Fig. 16*), and by Crowson (121). For most systems, however, η increases with ϕ in the full range of investigated $\dot{\gamma}$ (105, 108-110, 114, 121, 124). An example of this behavior is shown in *Fig. 19* for PS and PE filled with FG (11).

(3) An anomalous behavior of η is illustrated in *Fig. 20;* the addition of ϕ = 0.001 of glass powder (2μm) reduced the shear viscosity of PS from $1.46 \cdot 10^5$ (*P*) to $8 \cdot 10^4$ (*P*); i.e., by 45 percent. Similar effect was observed (113) for all 15 types of particulates dispersed in PS, PP, and elastomers. The authors suggested that the phenomenon originates in a reduced polymer segment density near the particulate surface; i.e., an extra free volume introduced by addition of the initial amount of filler.

Melt Elasticity

As reported in *Table 10,* four different methods were used to measure the melt elasticity of the filled polymers: N_1 = the normal stress difference, B = the die swell parameter, ΔP_e = the Bagley correction, and G' = the storage shear modulus.

The N_1 vs. σ_{12} plots provide a direct view into the different mechanisms of the flow of polymers filled with fibers (see *Figs. 21* and 22) and small particulates (see *Fig. 23*). For σ_{12} = const, in the first case, N_1 increases with ϕ (115, 125), in the second, N_1 decreases (97, 115, 126). For glass beads of diameter 10 and 36 (μm), N_1 remains unchanged.

Recently, η and N_1 were measured in a steady-state rotational mode for particulate-filled, maleic anhydride polyester resin (128). When 20 to 30 wt.% of high-

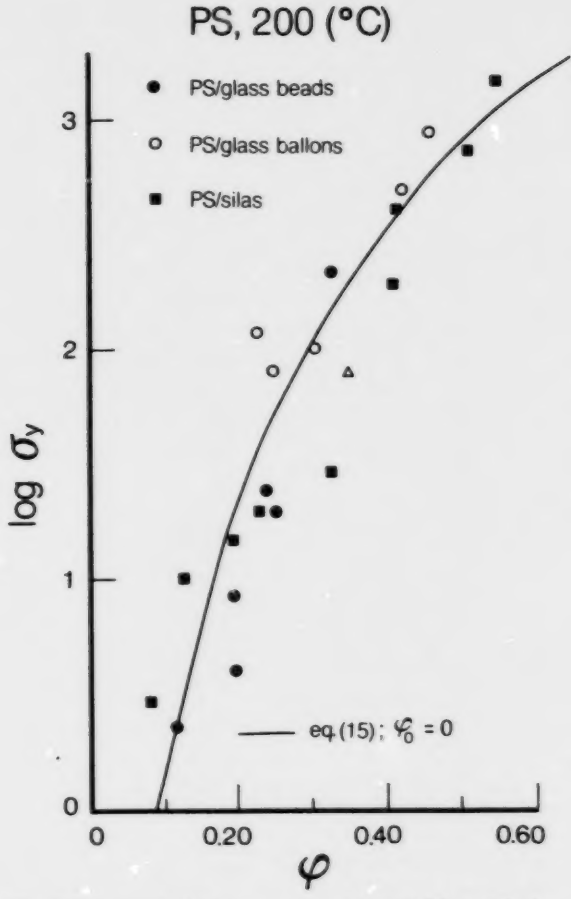

Fig. 18. Apparent yield stress σ_y vs. ϕ for PS filled with glass beads and balloons; line—Eq 15 with ϕ_0 = 0, points (111).

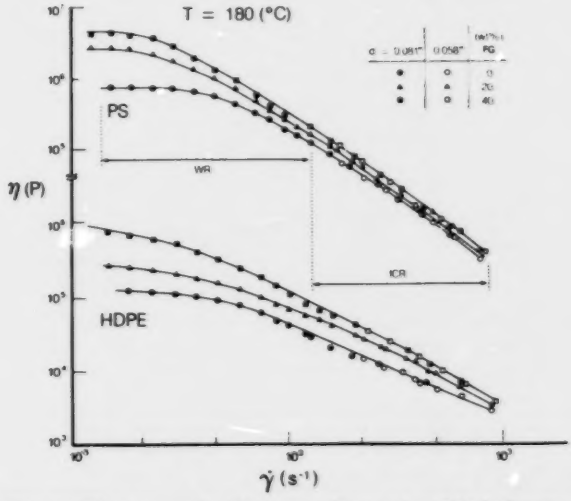

Fig. 19. Flow curves for PS (upper diagram) and high-density PE (lower diagram) at 180°C filled with 0, 20, and 40 wt.% of glass fibers (110). WR and ICR indicate the Weissenberg Rheogoniometer and Instron Capillary Rheometer, respectively.

density PE particulates (d = 40 (μm)) were added, negative values of N_1 were obtained. It was observed that $-N_1$ is an increasing function of σ_{12}, independent of ϕ

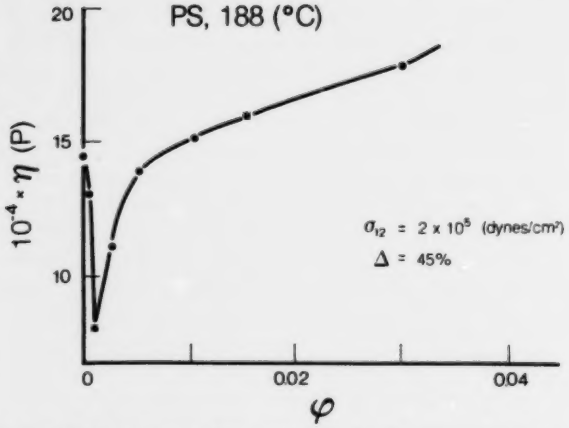

Fig. 20. Melt viscosity of PS at 188°C and at shear stress $\sigma_{12} = 2 \cdot 10^5$ (dyn/cm²) vs. ϕ of glass powder (113), Δ = 45% indicate the maximum depression of η.

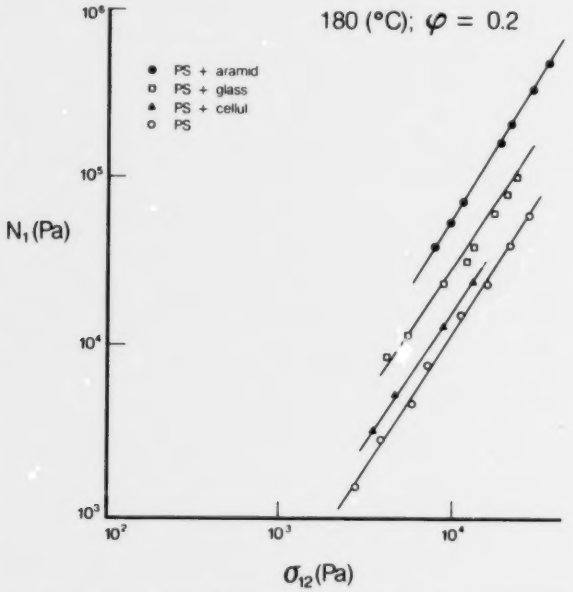

Fig. 21. N_1 vs. σ_{12} for PS at 180°C reinforced with ϕ = 0.20 of aramid, glass, and cellulose fibers. Data for PS are also shown (115).

and shearing history. Reversing the shearing direction or changing the shearing time did not affect this unusual behavior.

For neat polymers, the die swell measurements provide simple and useful means of extending the measurements of normal stress difference to the high range of $\dot{\gamma}$ (129). In *Fig. 24*, the recoverable shear strain

$$s = N_1/2\ \sigma_{12} \qquad (25)$$

is plotted as a function of $\dot{\gamma}$ for PS, PE, and PVC; here, the open or small points represent the direct N_1 measurements and the black or encircled points, the values calculated from B.

For filled systems, the correlation does not seem to be valid. In *Fig. 25*, B *vs.* $\dot{\gamma}$ is plotted (124). It can be seen that, for FG-filled polycarbonate melts, B de-

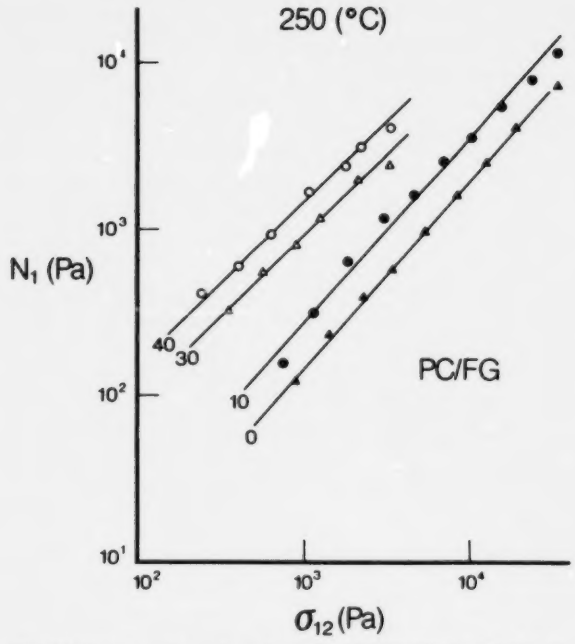

Fig. 22. N_1 vs. σ_{12} for polycarbonate at 250°C filled with 0.0, 10, 30, and 40 wt.% of glass fibers (124).

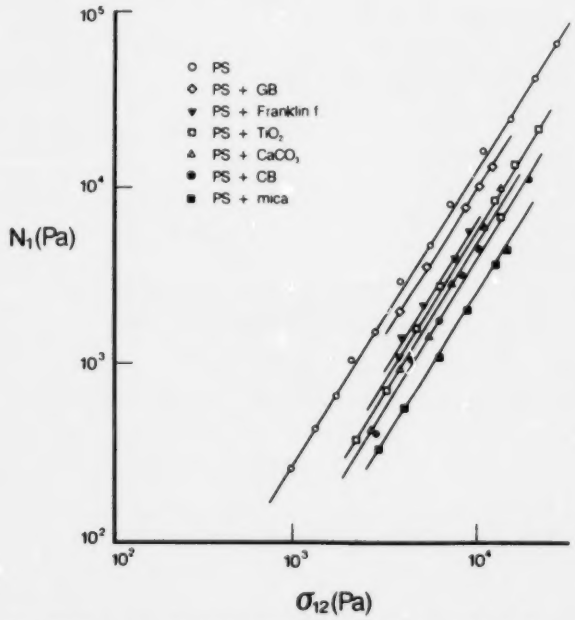

Fig. 23. N_1 vs. σ_{12} for PS at 180°C filled with ϕ = 0.20 of, from the top, PS, glass beads, Franklin fibers, TiO_2, $CaCO_3$, carbon black, and mica (115).

creases with ϕ in spite of the fact that N_1 increases (see *Fig. 22*). A decrease of B with ϕ was reported for PS/FG (108), PE/TiO_2 (109), PP/Talc (119), PP/FG, and polyamide 6,6/FG (121) systems. For PP/FG suspensions, the entrance pressure drop, ΔP_e, was observed (120) to increase with ϕ while, at the same time, B was observed to decrease (121). On the other hand, for PP/Talc (119), both ΔP_e and B were reported to decrease. In the absence of direct experimental evidence, one is tempted

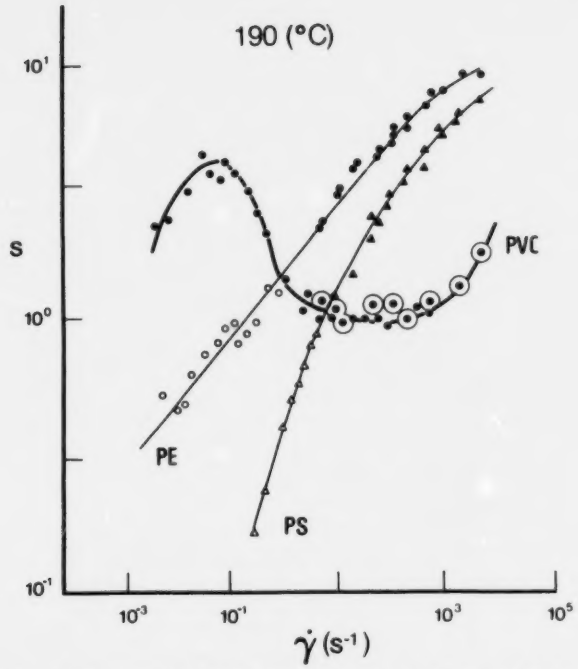

Fig. 24. Recoverable shear strain, s, vs. $\dot{\gamma}$ for PS, PE, and PVC melts. Open or smaller symbols calculated from N_1, solid or larger circles—from die swell (129).

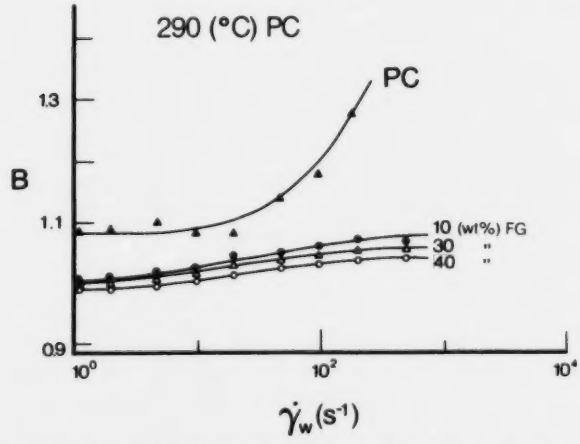

Fig. 25. Die swell ratio B vs. wall shear rate for polycarbonate, PC, at 290°C filled with 0, 10, 30, and 40 wt.% of glass fibers (124).

to speculate that the concentration dependencies of N_1 and ΔP_e paralleled each other, both being measures of the true elasticity of the matrix. The die swell, however, is a more complex phenomenon involving kinetics. A good, reliable set of data of all four measures of melt elasticity: N_1, B, ΔP_e and G', is badly needed.

Dynamic testing has been infrequently used to study the rheological behavior of filled plastics. The superiority of dynamic over steady-state flow method lies in the fact that the results are directly related to the structure of the material. One can easily visualize a situation where two samples cut from extruded material (one in the machine, the other in the transverse direction) will show different dynamic behavior in the melt. This, of course, will not occur for the steady-state flow methods, where the shear field will generate mophology pertinent to the given set of conditions.

In *Figs. 26* and *27*, the preliminary results of melt flow behavior of high-density polyethylene (PE) filled with 0, 25, and 60 wt.% of the surface-treated phlogopite (average flake diameter, 125 μm) are shown (130). For comparison, the apparent steady-state capillary viscosities are also included. It can be seen that an excellent agreement between η and η' for PE and for the sample containing 60 percent of mica was obtained, but the two sets of data for PE with 25 percent of mica did not superimpose. The reasons for selecting η' rather than η^* are: a better superposition for the neat resin and the absence of σ_y for PE in the $\eta' \times \omega$ *vs.* ω plot (the dependence η^*/ω *vs.* ω did indicate σ_y!). The correlation between the steady-state and dynamic rheological data has been previously discussed (131). The spread of data for 25 wt.% dependence at low frequencies is due to time of shearing effects, observed but not subtracted. It is likely that the disagreement between η and η' data for this sample originates in the time-dependent structures, in a manner similar to the one observed in *Fig. 13*. The yield stress, σ_y (dynes/cm^2), calculated from data shown in *Fig. 26*, obeys the relation:

$$\sigma_y = 1.2 \cdot 10^5 \, \phi^{1.42} \qquad (15a)$$

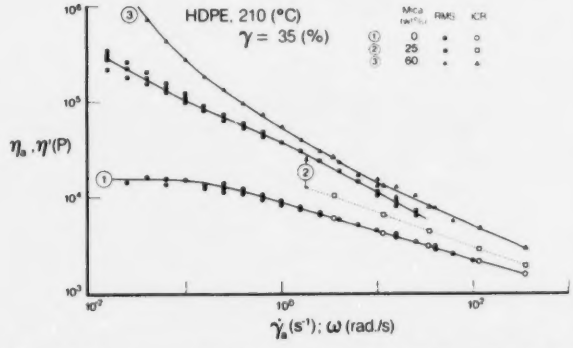

Fig. 26. Flow curves for high-density PE at 210°C filled with 0, 25, and 60 wt.% of mica. Data from capillary (η_a) and dynamic (η') tests (130).

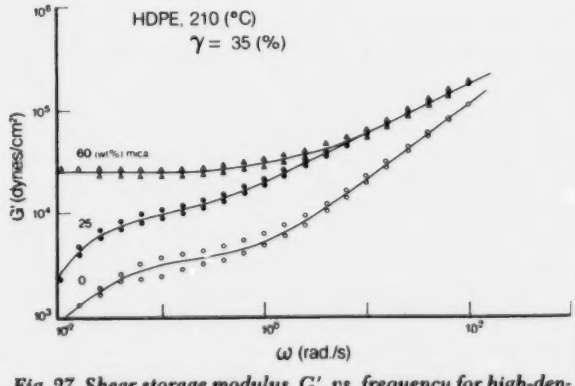

Fig. 27. Shear storage modulus, G', vs. frequency for high-density PE at 210°C and strain 35%, filled with 0, 25, and 60 wt.% of mica.

The shear storage modulus, G' (dyn/cm²) *vs.* ω is shown in *Fig.* 27 for the same three samples discussed above. It can be seen that, at low frequencies, the melt elasticity is proportional to the mica content. However, at higher range of ω, the $G' \neq G'(\phi)$. Note also that the sample containing 25 percent of mica shows an intermediate behavior between that of the "lightly crosslinked rubber" for 60 percent filled PE and "highly branched polymer melt" behavior of the neat PE (132). When the temperature is lowered, the rubbery plateau is pushed toward a higher value and lower frequencies, and the time-dependent anomaly of η' *vs.* ω observed for 25 wt.%-filled system becomes stronger (130).

Elongational Viscosity η_e. Data for styrene acrylonitrile copolymer (SAN) filled with 50 μm-glass beads indicated (104) that, for $\phi \leq 0.2$, the Trouton rule is obeyed. For the highest loading, $\phi = 0.363$,

$$\eta_e/\eta = 1.7 \pm 0.3$$

was found. By contrast, the systems containing submicron particles (116) are known to exhibit yield stress in both the shear and elongational flow. The ratio:

$$\sigma_{11,Y}/\sigma_{12,Y} = 1.2 - 1.9$$

was reported (116). This behavior is illustrated in *Fig.* 28. It can be seen that here, $\eta_e > 3\eta$, and that filler surface treatment has a profound effect on the low deformation rate behavior.

The elongational viscosities of fiber-filled polymer melts (108, 110, 115) can be summarized as follows: (a) because of the high yield stress, $\sigma_{11,y}$, the Trouton ratio, $\eta_e/3\eta$, for low elongation rates, $\dot{\epsilon}$, reaches a very large value (see *Fig.* 29); at high $\dot{\epsilon}$, by contrast with neat resins, the Trouton ratio for fiber-filled systems falls below one; (b) qualitatively, the η *vs.* $\dot{\epsilon}$ dependence for fiber- and submicron particle-filled polymer melt is the same, as can be seen by comparing the results presented in *Fig.* 29 with those *Fig.* 30; (c) whereas, for suspensions of particles in Newtonian liquids, η_e = const. over a wide range of $\dot{\epsilon}$; for those in polymer melts, η_e strongly depends on $\dot{\epsilon}$.

Theoretical Treatments. Theoretical treatments for filled polymer melts have been reviewed and discussed in recent publications (127, 133-135). The shear viscosity of concentrated suspensions in power-law fluids (including the yield) was calculated (135) using the cell theory. From constitutive equations, the stress tensor for suspensions of hard spheres (127) and fibers (133) has been derived. The calculations (115) allow for a good fit of η and η_e for particle-reinforced polysty-

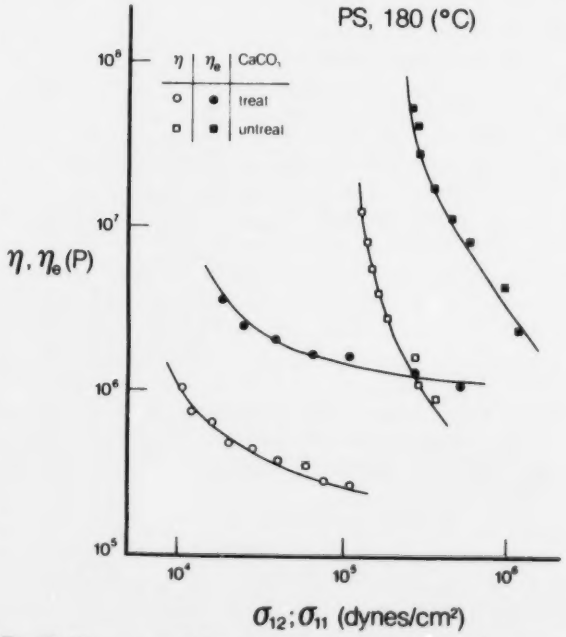

Fig. 28. Shear, η, and elongational, η_e, viscosities vs. shear and elongational stress, respectively, for PS at 180°C filled with 30 wt.% of treated and untreated $CaCO_3$ (116).

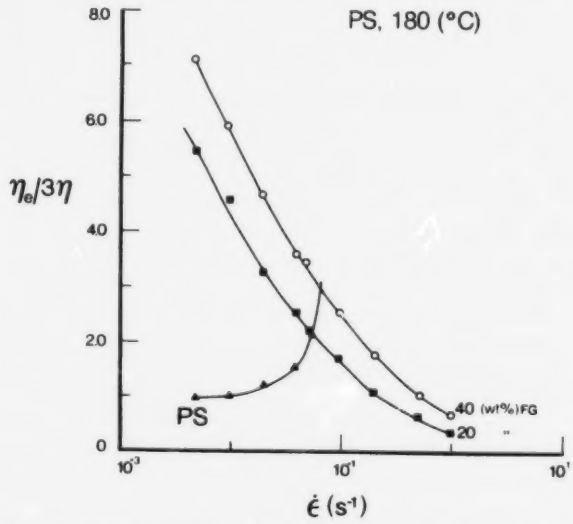

Fig. 29. Trouton ratio vs. deformation rate for PS at 180°C filled with 0, 20, and 40 wt% of glass fibers (108).

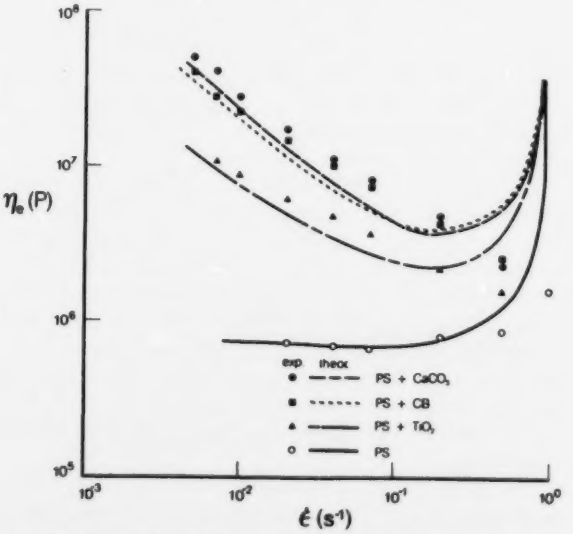

Fig. 30. Elongational viscosity vs. elongation rate for PS at 180°C filled with, from the top: $CaCO_3$, carbon black, TiO_2, and for pure PS. The curves are theoretical (115).

renes (see *Fig. 30*). The theory requires experimental determination of the yield stress. Through the time-dependent yield function, the thixotropicity can also be incorporated. The derivations for fiber-filled polymer melts (133) provide a fair representation of η, η_e, transient viscosity, N_1, and the second normal stress difference, N_2. The rheological behavior of both the particulate- and fiber-filled systems can be predicted (134) from the Lodge rubber-like model with a strain-dependent memory function. The time dependence can be calculated from the dynamic moduli in the linear viscoelastic region. The derivation allows the calculations of η, η^*, N_1, N_2, and the transient behavior.

PROCESSING AND RHEOLOGY

The filled polymer melts are processed primarily by extrusion and injection-molding methods. In commercial applications, it is frequently desirable to mix different types of fillers/reinforcing agents in order to secure the best packing efficiency (59, 136). Using numerical methods (136), combinations of up to five different particulate and fibrous materials in the range of sizes from 0.5 to 250 μm may be optimized. These preparations can significantly reduce the raw material and processing costs, reduce wear of the equipment, ease the processing, and improve the product. At high loadings and under the normal processing conditions, the key rheological property is the shear viscosity. With hindered rotation of particles, a plug flow profile and zero normal stress differences are to be expected. Under those circumstances, the time dependence of η and the skin-core flow structure are observed. This mean that, for efficient processing of highly filled plastics, the compounding should be immediately followed by the processing step: extrusion, injection- or transfer-molding, spray-up, etc.

One of the basic problems in compounding is the reduction of aspect ratio of the fibers and flakes (114, 137). This can be partially prevented by: surface coating of particulates, in order to minimize the necessary mixing time; incorporating the particulates into polymeric liquids at the highest possible temperature, to reduce η; using twin-screw extruders, impinging mixers, or other types of equipment where mechanical or high-shear breaking action is limited.

Extrusion. Extrusion is the basic plastic processing operation. For analysis of extrusion of filled materials, the standard methods of calculation (137-140) can be used. In a single-screw extruder (108), the fiber breakage was found to be related to the screw speed and η. Most of the damage occurred in the melting zone, and the degree of damage increased with a decrease of temperature and increase of molecular weight. Using milder extrusion conditions (i.e., low screw speed, low η) did reduce the damage, as well as the degree of dispersion.

The presence of particulates has an effect on melt fracture (140, 141); it increases the critical shear stress at which it occurs and decreases its intensity.

Injection Molding. Injection molding requires higher $\dot{\gamma}$ and lower η than extrusion does. This means that lower loading of particulates or low viscosity suspending liquids are preferred; i.e., the Reinforced Reactive Injection-Molding (RRIM) is the ideal technology for the filled plastics. Alternatives are transfer-molding (142) or spray-up (136). Since the fiber orientation is desirable, the elongational and shear fields must be provided by a proper channel profile. It is important, in this case, that the fiber concentration ($\phi \leq 0.4$) and the aspect ratio ($p \cong 25$) allow for the free rotation of particles.

The importance of mold geometry and temperature was demonstrated in a study of mold filling by PP, PP/glass blends, and PP/FG (143). While the geometry determined the extent of fiber orientation, the temperature determined the thickness of the wall skin; i.e., the size of the core channel and, in effect, the velocity profile in the mold. This work was continued (144) in simple end-gated molds where the effect of the processing conditions and rheology on fiber orientation were examined. It was found that high injection speeds favored a transverse alignment of fibers in the core, while slow speeds favored the longitudinal orientation. Moldings produced at high speeds had a glossy surface, while those at low speeds had a matte surface.

There is little information on the effects of rheology and processing on the flow orientation of mica flakes in polymers (105, 145). During flow through tubes (31) of concentrated suspensions in Newtonian liquids, skin/core structure was observed. In the core, both fibers and discs preferentially aligned longitudinally; i.e., in both cases, with the longest dimension in the flow direction. In extrusion of mica-filled PP (105), the opposite effect was observed; near the wall, the flakes were parallel to the flow direction while, near the center, they were perpendicular. A similar structure was observed during injection-molding (145), but there the core anisotropy was very low.

Machine Wear. Machine wear during processing of filled materials is quite high (146, 147). Both corrosive and erosive wear were reported. The corrosive damage, due to thermal decomposition of a sizing agent, caused an increase of barrel bore diameter and a corresponding decrease of the screw diameter, both occurring at the front end. The abrasive (or erosive) wear is most severe in the melting zone of the extruder, where η and the pressure are the highest. The wear also increases with filler hardness, particle size, and aspect ratio, and the extent of agglomeration. It was reported that modification of process conditions, primarily in respect to the rheological conditions of a filled polymer melt, increased the lifetime of the equipment by a factor of 10. Work on these important aspects is being carried out at the Industrial Materials Research Institute of the NRCC.

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DISCUSSION

L. P. Hebert. You mentioned that, in extrusion of mica-filled propylene, mica tends to migrate toward the center of the capillary tubes. Well, do you have an explanation for this?

L. A. Utracki. There is a very good explanation based on hydrodynamic calculations. For instance, Professor S. Mason from McGill has calculated theoretically, and demonstrated in ingenious experiments, the migration of solid particles toward the center of the stream. His work was conducted primarily on suspensions in Newtonian liquids, but the conclusions should be of general significance. The orientation of particles may be different in Newtonian than in a viscoelastic fluid; Mason's data indicate that flakes and fibers in the center of a capillary are aligned with the longest axis parallel to the flow lines, whereas the observations made independently by Professor Woodhams and by Bernard Sanschagrin show a perpendicular orientation of mica flakes in polymeric media, though the effect may depend on the rate of shear. A thorough theoretical analysis of the orientation as a function of shear and normal stress would be very desirable.

G. C. Hawley. One of the most serious problems in the extrusion of mica-filled plastics is the surface roughness. This must be related to the flow behavior. Could you comment?

L. A. Utracki. Indeed, the roughness is related to the rheology. We also observed very serious surface roughness of mica-filled polyethylene. The phenomenon is most likely related to the relatively slow, hindered rotation of flakes in comparison to the rates of shear on the die wall. What to do about this? There are four possible methods: (1) increase the rate of flakes rotation (e.g., by increasing the temperature of the die and/or reducing the friction between the flakes and the die) (I have successfully used dies with changeable plastics inserts); (2) extend the available time for the flake to orient by slowing down the extrusion rate, extending the length of the die, and/or streamlining the entrance to the die; and (3) coextrusion or post-extrusion coating. These are possible methods for improvements, proposed on the basis of experience. They may work or not, depending on the case. What we need is a thorough knowledge of the mechanism of flake orientation at high solid concentration combined with the mathematical simulation of flow through channels of different profiles.

J. M. Charrier. I would like to make a general comment. What you read nowadays in technical, not so much the scientific, literature is extremely confusing. For instance, you read about people doing studies on injection-molding of nylon-reinforced with mica. They say that increasing the back pressure or the holding time will do this and that. Now, if you go to another paper written by someone else on filled poly(carbonate). you find something quite different; increasing the mold temperature or decreasing the holding pressure results in a completely different effect. Obviously, the process is not well-understood. There are so many parameters! I suspect that a change in back pressure or screw speed may also lead to a change in fiber length. Maybe not the orientation alone, but also the total structure, morphology, should be considered. It is very confusing. At one point, I collected several technical papers and tried to draw general conclusions in view of teaching. I found it impossible. For industry, it may be useful to get simple, empirical advise that may work for a specific case. However, one should try to provide a more general answer.

L. A. Utracki. I fully agree with you; I think that the industry is mature and sophisticated enough to deserve better answers. In the long term, understanding will ease the development of new materials and processes. I think that we at NRC are particularly well-suited to do this job; it will require integration of the practical know-how of industry with the results of fundamental studies carried out in academia.

Hot-Rolling and Forging of Mica-Filled Polyolefins

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As in the case of fibers, the mechanical properties of plastic composites containing mica flakes are extremely sensitive to flake orientation in the direction of an applied stress, so that even a small angular displacement can cause major reductions in the strength, modulus, and fracture toughness. In order to encourage parallel alignment of mica flakes in a thermoplastic composite, two methods of flow orientation were examined. In the first series, rectangular billets of mica-filled, high-density polyethylene were hot-pressed in order to cause longitudinal melt flow in a narrow channel. A parallel series of experiments was also carried out with mica-filled polypropylene in which the composite was extruded and calendered into a thin, continuous strip. In both processing techniques, the resulting extensional flow produced large increases in the tensile and flexural properties. The performance of the mica-filled polypropylene was limited by its tendency to fibrillate during rolling. Drop-impact measurements recorded a four-fold increase in fracture toughness. The increased tensile and flexural properties were attributed to both the greater degree of parallel alignment of the mica flakes and the increased molecular orientation in the direction of flow. Such flow orientation methods appear necessary if the full benefit of mica-flake reinforcement is to be achieved.

INTRODUCTION

It is generally recognized that, when a crystalline polymer is subjected to rolling, drawing, or calendering, the resulting molecular orientation produces marked changes in the mechanical and physical properties (1). When the polymer contains short fibers, the rheological history of the mixture will also influence the spatial orientation behavior of the dispersed fibers in the polymeric resin and, therefore, the fiber orientations in a molded composite may be controlled to some degree through appropriate modification of these flow patterns during processing (2, 3). The combined effects of both molecular and fiber orientation brought about by such processing greatly magnifies the resulting mechanical and physical properties of the composite. The sensitivity of both tensile strength and Young's modulus with respect to uniaxial fiber orientation is well-known, and fibers that are oriented just 10° off axis to an applied stress can reduce strength and modulus by 40 percent (4). It is important, therefore, that fibers be precisely oriented in the direction of applied stress for maximum efficiency. In a similar manner, the spacial orientation of flake-type fillers in a thermoplastic resin are responsive to flow history during processing, and the resulting flake orientations can greatly alter the mechanical and physical properties of the composite. Harbourne and Zboril (5) have used mica as a filler in blown polyethylene film to manufacture food packaging films, having reduced permeability to air and water vapor. In this example, the orientation of the mica was brought about by biaxial stretching of the polyethylene film, which imparted a significant increase in the modulus of elasticity and a corresponding decrease in the tensile strength and ultimate elongation.

Earlier studies (6-8) had shown that, when mica is admixed with a finely divided thermoplastic powder and compression-molded, the resulting strength and modulus values were much greater than those attainable by injection-molding procedures. Microscopic examination of the injection-molded specimens revealed a typical whorl-type pattern, with mica flakes near the mold surface having a more uniform, parallel, overlapping configuration in the direction of flow, whereas the mica flakes in the central portion were oriented perpendicularly to the flow direction. This nonuniform flake orientation was thought to be partly responsible for the large difference in strength and modulus between injection-molded specimens and samples fabricated by compression-molding (either thermoplastic or thermosetting composites).

In order to encourage a greater degree of parallel flake orientation, rectangular cast billets of high-density polyethylene containing mica were hot-pressed in a special open-ended mold (in the shape of a rectangular channel) to cause longitudinal flow. This forging process simultaneously reduced the thickness and in-

creased the length of the billet as it was forced to flow along the open channel (*Fig. 2*). A progressive increase in the modulus and strength of the elongated billet occurred as the thickness was reduced by hot-pressing.

In a second series of experiments with mica-filled polypropylene, a hot extrudate was rolled to produce a continuous thin strip. The tensile and flexural properties again showed a similar pattern of behavior as the thickness of the strip was reduced. The following section describes these two processing techniques in detail.

EXPERIMENTAL

Hot-Pressing

Polyethylene (Dupont Sclair 2909) was compounded with mica (Marietta Suzorite 60H) in a twin-screw Brabender Prep-Center and pelletized in a Brabender granulator prior to extrusion and melt casting. Rectangular billets of the mica-filled, high-density polyethylene were prepared by extruding the melt into a rectangular die (*Fig. 1*), which was 20.3 cm long and 4.48 cm square. The melt was allowed to flow into the bottom of the mold until it filled the cavity and was then allowed to cool. After removing the now solid casting from the mold, it was placed in a press with a rectangular channel 5 cm wide, 8 cm deep, and 20 cm long, open at both ends (*Fig. 2*). Prior to hot-pressing, the cast billet was preheated to its softening point near 115°C and then placed in the mold, which was heated to the same

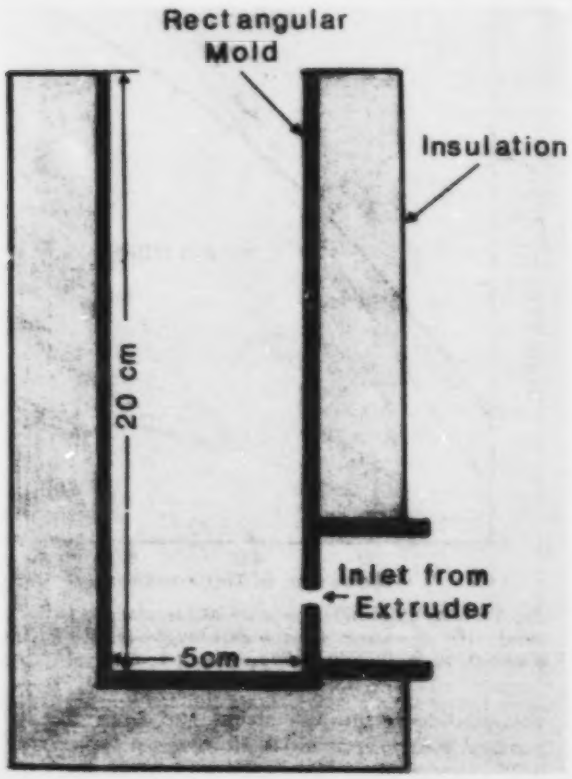

Fig. 1. Small rectangular castings could be simply produced by extruding molten mica-filled polyethylene into a rectangular aluminum mold and allowing it to cool.

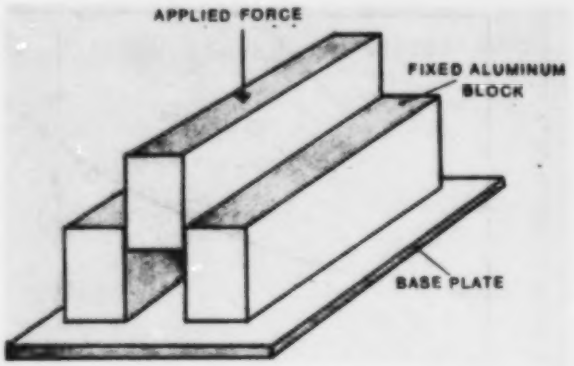

Fig. 2. The rectangular blocks of mica-filled polyethylene were hot-pressed in a close-fitting aluminum channel in order to induce longitudinal flow.

temperature. The billets were then subjected to a pressure not exceeding 13.8 MPa, so that the thickness was reduced and the polyethylene billet was forced to flow longitudinally via the open ends of the mold. Stops were placed in the press to limit the extent of compression, so that the final thickness of the pressed billet could be controlled.

After cooling the mold and removing the hot-pressed billet, flexural (ASTM D790), tensile (ASTM D638), and impact measurement were obtained from sections cut from the billet so that changes in mechanical properties could be followed as the thickness of the billet was progressively reduced.

Calendering

Mica (Marietta Suzorite 200 HK) was compounded with polypropylene (Hercules 6823 extrusion grade) in a twin-screw Brabender Prep-Center and subsequently pelletized for calendering. The mica was previously surface-treated with a silane-coupling agent (Dow Corning Z-6032). The compounded resin was then placed in the hopper of a two-stage compounding extruder (L/D 24:1, screw dia. 19 mm) and extruded through a circular orifice (6.35 mm diameter) at temperatures between 200 and 225°C into a two-roll, Teflon-coated calender with twin heated rolls. Heated oil was circulated through the rolls to maintain the roll temperature between 80 and 90°C. The rolls could be adjusted with screws to control the gap between the rolls and the thickness of the calendered extrudate. The resulting calendered strip was approximately 5 cm wide and 1 to 3 mm thick.

Longitudinal sections were cut from the calendered strip for tensile and flexural measurements (ASTM D790-71).

RESULTS

Hot-pressing the mica-filled polyethylene billet produced an increase in the tensile and flexural properties, as shown in *Figs. 3, 4,* and 5. Even when the billet had been compressed to 25 percent of its original thickness, the modulus and strength values were still increasing. The flexural modulus was particularly sensitive to the reduction in thickness, as is evident from

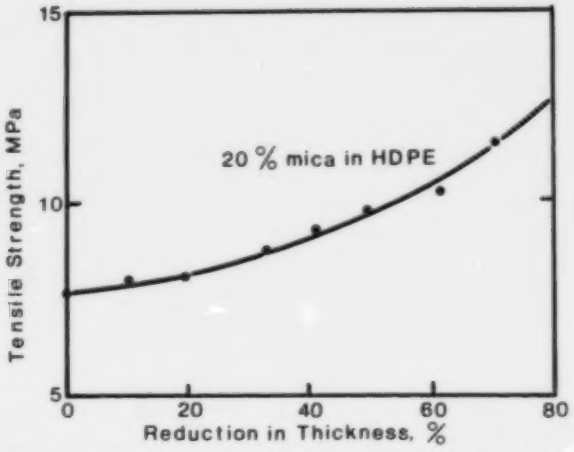

Fig. 3. Hot-pressing a mica-filled billet of high-density polyethylene produces a progressive increase in the tensile strength parallel to the direction of flow.

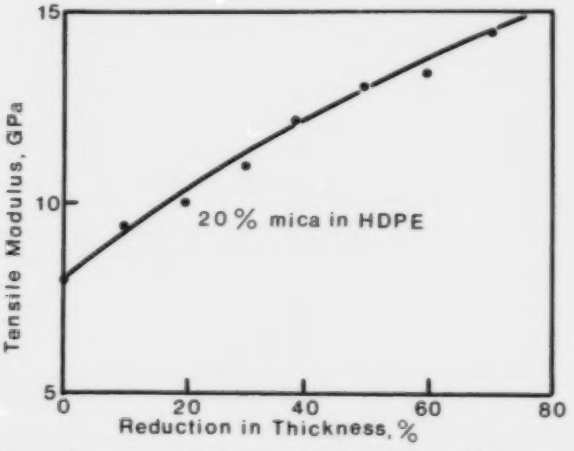

Fig. 4. A corresponding increase in the tensile modulus occurs during hot-pressing. The increase is even more pronounced when the mica concentration is increased to 30%.

Fig. 5 (12-fold increase), whereas the tensile modulus is less sensitive and appeared to be approaching a limiting value. Obviously, the two moduli values (flexural and tensile) must approach the same maximum limiting value which, from compression-molding experiments, appears to be near 20 GPa (6, 7) at this mica concentration. Further reduction in the thickness of the billet, perhaps to 1/20th of the original thickness (95 percent thickness reduction) might be required to achieve this limiting value in practise.

Impact toughness was estimated from circular disks (0.60 cm thick by 5 cm diameter) using an instrumented Dymetron 301 Impact Tester (Detroit Testing Machine Co.). This modified-dart-impact test revealed a parallel increase in fracture energy as the billet was reduced in thickness and was almost four times tougher when reduced to 25 percent of its original thickness. The fracture toughness, measured by the Izod impact test, shows an opposite trend.

Similar changes in the mechanical properties were observed when mica-filled polypropylene was extru-

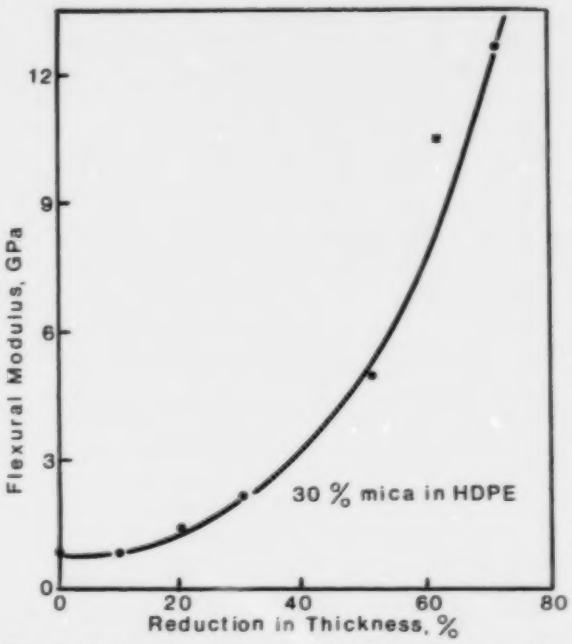

Fig. 5. Hot-pressing has a considerable influence on the flexural modulus of mica-filled, high-density polyethylene. This is typical of most mica-filled thermoplastics and thermosets.

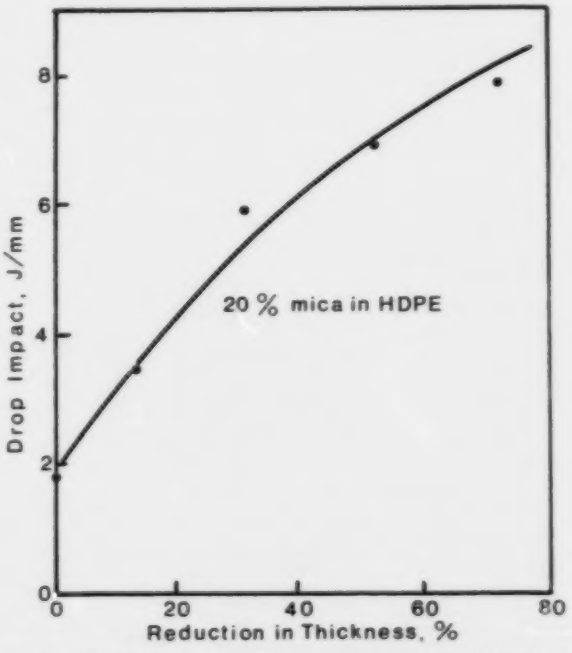

Fig. 6. The drop-impact (Dymetron 300) results also indicate a substantial increase in panel or disc toughness. The Izod impact tests normally follow the opposite trend.

sion-calendered into thin strips. The results are summarized in *Figs. 7, 8,* and 9. However, polypropylene, unlike polyethylene in the previous hot-pressing experiments, tended to spontaneously fibrillate during the rolling process, producing many voids (*Fig. 10*). This formation of voids greatly reduced the flexural stiff-

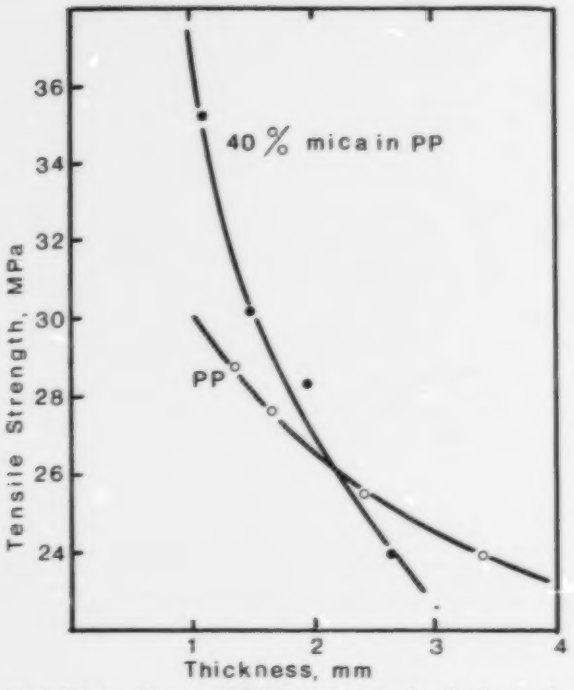

Fig. 7. The tensile strength behavior for calendered polypropylene containing mica follows a trend that is similar to that of hot-pressing. Note that calendering also increases the strength of unfilled polypropylene.

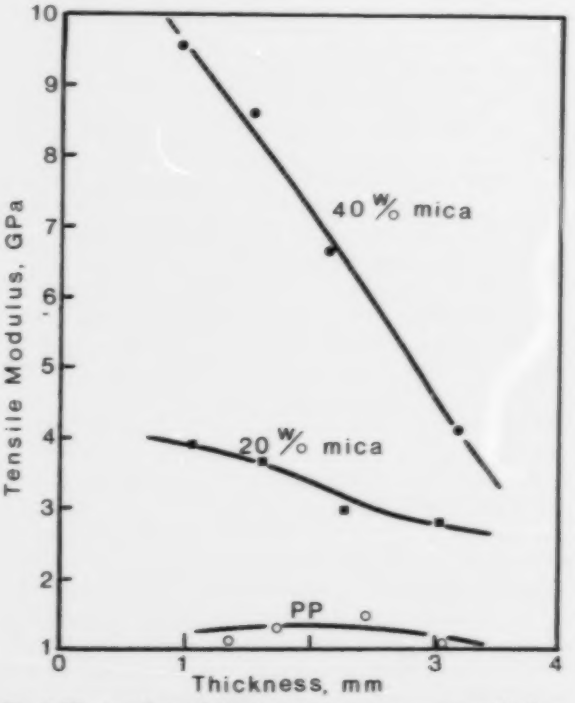

Fig. 8. The tensile modulus increase is more pronounced when mica is present. Note that unfilled polypropylene does not respond to hot-rolling in the same way as cold-rolling.

ness and caused the flexural values to decline after reaching their maxima (*Fig. 9*). Note, however, that the fibrillation did not adversely influence the tensile

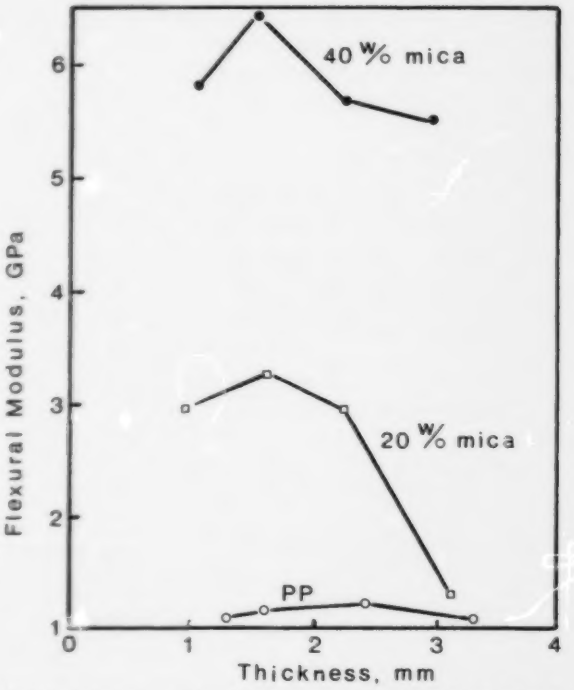

Fig. 9. Attempts to calender the molten-mica-filled polypropylene frequently caused fibrillation and void formation. Consequently, the flexural properties did not increase as expected.

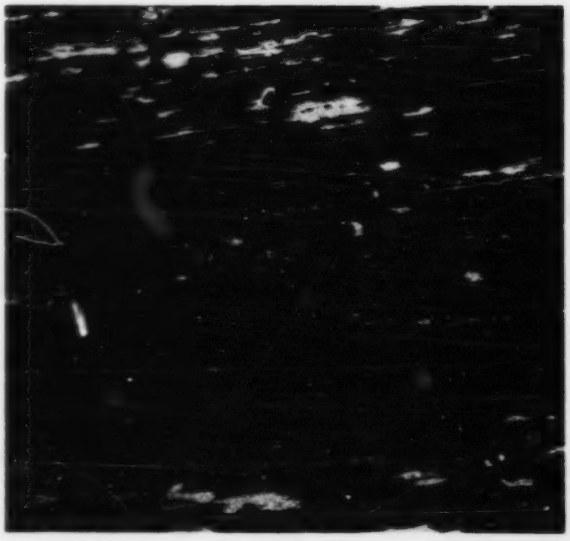

Fig. 10. This scanning electron microscope photograph (61 ×) clearly reveals the parallel striations caused by fibrillation of the polypropylene during rolling.

values (*Figs. 7* and *8*), which continued to increase as the thickness of the calendered strip was further decreased. All these measurements were conducted in the rolling direction. Future investigations will explore the property changes at even greater reduction ratios, analyze changes in the transverse direction, extend the process to solid-state rolling, employ improved grades of mica, and assess the influence of processing aids, vis-

cosity modifiers, and coupling agents on the overall performance.

DISCUSSION

The process of rolling or drawing a flake-filled composite tends to align the flakes parallel to the direction of flow, as is illustrated schematically in *Fig. 11*. This effect is also apparent in the sectional photographs taken before and after rolling (*Figs. 12* and *13*), in which

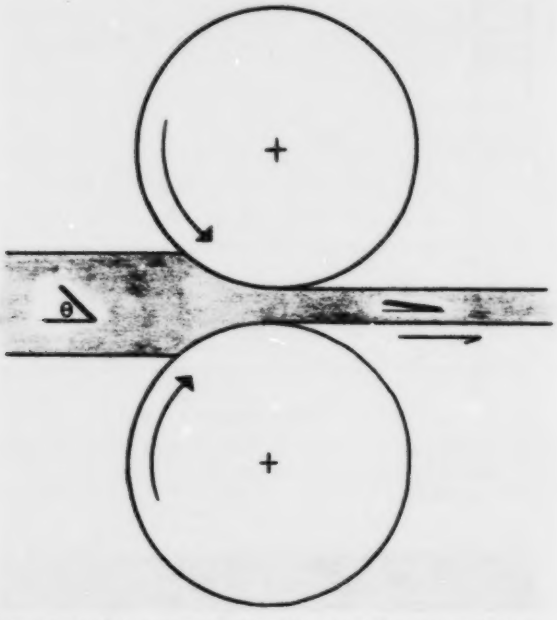

Fig. 11. In this exaggerated profile, the influence of thickness reduction on flake orientation is illustrated. The flake angle in the transverse direction will be similarly influenced by transverse flow behavior.

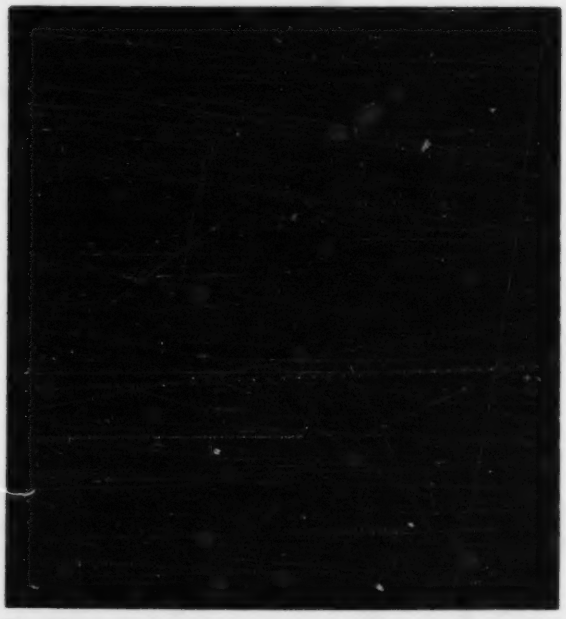

Fig. 12. A polished cross-section of the extruded mica-filled polypropylene shows the poor parallel orientation of the flakes prior to calendering.

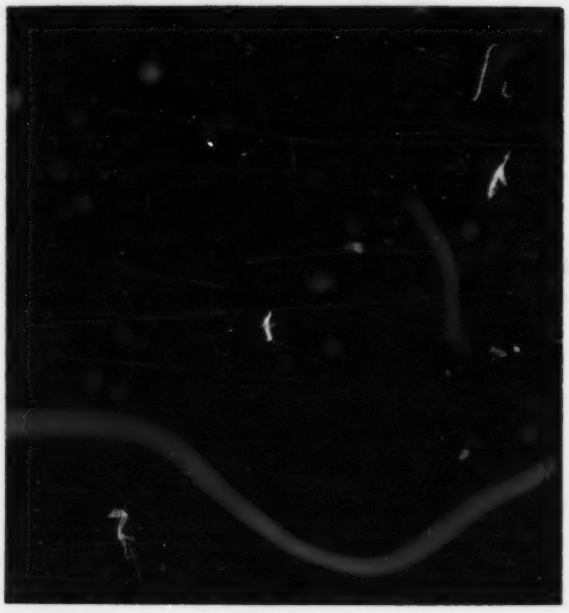

Fig. 13. After calendering, the mica flakes have assumed a more parallel overlapping distribution.

only the edges of the individual flakes can be seen in the polypropylene matrix. This partial alignment of the mica flakes can have a profound effect on the mechanical properties, both in the direction of rolling and in the transverse direction. The influence of fiber orientation on the strength and modulus properties of various composites has been adequately treated in several textbooks (3, 4, 9, 10), where it has been shown that these properties have a pronounced dependence upon the angle of fiber orientation (*Fig. 14*). It is likely that flake composites will follow a similar trend, the angular dependence in the case of a flake involving both a longitudinal and a transverse orientation. The extreme sensitivity of the strength and modulus to the angle of flake orientation, particularly for small angles, emphasizes the necessity of having large thickness reduction ratios (greater than 10) in order to more closely approach the optimum level of performance. Since it is usually difficult to achieve large reductions in sheet thickness in a single pass by rolling, particularly in the solid state, multiple passes would be necessary to attain larger reduction ratios. This stepwise reduction in dimensions is analogous to the multiple rolling of steel or the drawing of fine wires in stages.

Since the rolling process can also produce a major alteration in molecular orientation and the disposition of the crystalline lamellae that comprise the polyolefin matrices (1), the altered matrix properties can also contribute to planar reinforcement through increased stress transfer at the resin flake interface.

CONCLUSION

Normal extrusion or injection-molding processes tend to disrupt the parallel orientation of mica-filled thermoplastics so that the tensile and modulus values are decreased. When such composites are subjected to

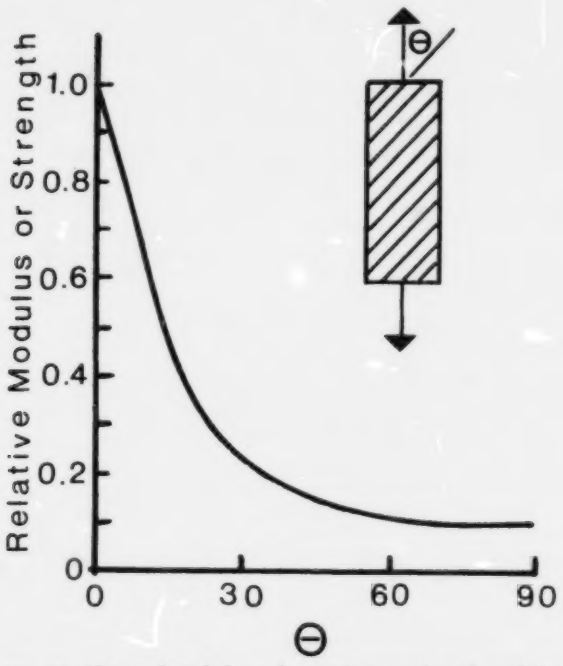

Fig. 14. The predicted dependence of strength and modulus upon fiber orientation angle follows the same pattern for flake composites.

extensional flow, as in rolling or drawing processes, parallel flake orientation is encouraged, and the tensile and modulus properties show a marked increase in the direction of orientation. The impact toughness also shows a corresponding increase. These preliminary results suggest that even greater tensile and modulus values can be expected as the draw ratios or thickness reduction ratios are further increased. The availability of improved grades of mica with larger aspect ratios and improved coupling will also contribute to greater performance. The rolling process can produce low-cost sheet materials having attractive lightweight structural efficiencies for use in thermoforming or solid-phase-forming processes.

ACKNOWLEDGMENT

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DISCUSSION

G. C. Hawley. On that STX table that you presented, were the data for Nylon 66 and polypropylene?

R. T. Woodhams. The table (not shown in text) shows a comparison between mica-filled polypropylene and Allied STX, the latter being a glass-fiber-reinforced nylon 66 stampable sheet material.

L. P. Hebert. Why did the drop test and Izod impact test give different results?

R. T. Woodhams. The two impact-toughness tests are difficult to compare, since they involve very different fracture processes. Both tests are sensitive to flake orientation and surface imperfections (scratches, notches). The notched Izod test, which was used in these experiments, was performed on molded bars having very sharp notch tips, so that fracture initiation energy was small or negligible. The dart impact test (measured on a Dymetron 300 Impact Tester using circular disks) involved a more complex fracture pattern, with a large energy contribution attributable to crack initiation and yielding. These two fracture tests reflect independent responses to particular types of impact that may be encountered in service.

L. P. Hebert. Does the Szego Grinder work with metals as well?

R. T. Woodhams. Yes, the Szego mill is currently being used by Professor Olev Trass to grind metals. Even refractory substances, such as tungsten carbide, may be ground to submicron dimensions.

L. A. Utracki. By thinning down the specimens via calendering, you are able to improve orientation of both the flakes and macromolecules. One would expect that you have aligned crystallinities of the polymers and increased total crystalline content. It seems that your work is related to what Andrew Garton was saying today. You showed a much steeper increase of modulus and strength in the presence of mica than without mica. I wonder if this effect is due to increased nucleation, which Andrew demonstrated, or to the reinforcing mica effect, per se.

R. T. Woodhams. The combined influence of molecular orientation and flake orientation on the mechanical properties is certainly much greater in the presence of mica than in the absence of mica. Although the mica may act as nucleating agent, it is likely that the calendering effect partially aligns the polypropylene crystallites and polymer chains in the calendering direction so that the stiffened matrix contributes to a more efficient stress transfer with the mica flakes. The calendering action will also increase the crystalline content of the matrix.

Properties and Economics of Mica-Reinforced Plastics Related to Processing Conditions

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Upgrading mica by increasing aspect ratio and coupling efficiency and combining mica with fibers has led to new uses as a reinforcement for thermoplastics and thermosets. The greatest growth in mica use has been in the thermoplastics, such as polypropylene and thermoplastic polyesters. Effects to be expected from using mica as a reinforcement include improved tensile and flexural strength, much-increased dimensional stability and heat resistance, enhanced stiffness and electrical resistivity, and reduced permeability to gasses and liquids. Major parameters that influence the composite properties include the mica flake size, orientation, aspect ratio and volume fraction, coupling efficiency, and crystallinity of the polymer matrix. Mica composites are molded from direct blends or are precompounded in the manner used for fillers. Mica-reinforced polypropylene (PP) is cost-effective in replacing glass-fiber-reinforced PP and may even substitute for glass-reinforced Nylon 66 in some applications. Markets for fillers for plastics are expected to grow faster than for the base polymers due to low cost, availability, and low energy utilization. Mica is expected to be one of the fillers with the highest market growth rate.

INTRODUCTION

Background of Mica in Plastics

Mica has long been known as a suitable filler for plastics. The largest use was as a filler in phenolic molding compounds to increase the dielectric strength and resistivity. Mica has been used for several years in polyester and epoxy casting resins for potting and encapsulation of electrical components. The chief improvements conferred by mica in the latter end use are:

- increase in impact resistance
- increase in thermal shock resistance
- decrease in cracking
- decrease in settling of fillers
- lower costs

Mica is regarded as the best filler for epoxies where high dielectric strength is required (1). In polyester resins, mica gives the lowest coefficient of thermal expansion of the fillers compared in *Table 1*. Retention of insulation resistance of epoxy castings when exposed to high temperatures and humidities is improved by surface treatment of the mica (2). All the above work was done, generally prior to 1973, on muscovite mica of small-aspect ratio (lower than 30).

A major breakthrough occurred after 1973 and included the publication of work showing that the physical properties of mica-filled composites can be improved markedly by increasing the aspect ratio of the mica in order to obtain values as high or higher than can be had with glass fiber reinforcement (3). Woodhams obtained aspect ratios as high as 300 by ultrasonic delamination of muscovite and phlogopite mica.

Subsequently, the Suzorite Mica Group (joint venture of Martin Marietta and Laviolette Metallurgical and Mineral) developed a mechanical method to produce commercial quantities of phlogopite mica with aspect ratios in the range 50 to 120 (4, 5).

Classes of Resins Influenced by Mica

Research b the Suzorite Group and others has shown high-aspect-ratio mica to be an effective reinforcing filler for the following polymers:

Thermosetting Polymers	References	Tables
Epoxy	1	*Table 1*
Polyester	1, 6, 7	*Tables 1 and 2*
Polyurethane (PU)	17, 18	
Phenolic	8, 12	
Thermoplastics		
Polypropylene (PP)	9, 10,11, 13	*Tables 12, 13, and 14*
High Density Polyethylene (HDPE) and Copolymers	12, 13	*Tables 15, 16, and 17*
Poly(butylene terephthalate) (PBT)	10, 12	*Tables 3, 4, 5, and 7*
Poly(ethylene terephthalate) (PET)	13	*Tables 4, 6, and 9*
Poly(4-methyl-1-pentene) (TPX)	13	*Table 20*
Nylon 66	12	*Table 18*
Styrenics	10, 12, 13	
Poly(vinyl chloride) (PVC)	13	*Table 19*
Poly(vinylidene fluoride) (PVDF)	13	
Acrylonitrile-butadiene-styrene (ABS)		*Table 8*
Polystyrene		*Tables 10 and 11*

Mica has a polar surface and is wetted by polar polymers, without coupling agents. In order to improve bonding with such polymers as PP and HDPE, the Suzorite Group developed Suzorex NP grades of high-aspect- atio mica, based on silanes and other coupling agents (10, 14).

High-aspect-ratio mica with a polar silane treatment was developed to enhance physical properties of polymers such as polyamides, polyurethanes, and polyesters (15).

Table 1. Effects of Several Fillers on Properties of Epoxy and Polyester Resins

	Epoxy resins				Polyester resins				
Property	Unfilled	Calcium carbonate	Mica	Glass	Alumina	Mica	Glass	Calcium carbonate	Unfilled
Coefficient of linear expansion*	72	57	43	—	70.5	65	70	81	97
Thermal conductivity watts/in.²)(°C)(in.)	0.008	0.014	0.012	0.012	0.0109	0.0074	0.0073	0.0069	0.0065
Water absorption, mg	24	20	22	24	60	50	40	50	50
Specific gravity	12	15.8	14.1	15.2	18.7	13.8	15.5	15	12.3
Compressive strength, psi	15,900	7,540	5,700	—	26,600	19,600	25,000	18,500	18,000
Tensile strength, psi	9,700	6,000	5,650	—	3,700	5,000	5,000	4,250	7,000
Dielectric strength, volts/mil	320	370	420	370	270	400	380	280	250-300
Brinell hardness (500-kg load, 10-mm ball)	—	—	—	—	76	49	49	65	49
Power factor, tan δ, Mc									
1	0.029	0.026	0.035	0.026	0.0194	0. 0213	0.0165	0.0173	0.018
10	0.029	0.026	0.034	0.026	0.0188	0. 0204	0.0171	0.0171	0.031 (at 1 kc)
20	0.028	0.026	0.032	0.026	0.0183	0. 0197	0.0170	0.0170	0.045 (at 50 cps)
50	0.026	0.025	0.030	0.025	0.0176	0. 0185	0.0165	0.0167	
100	0.020	0.023	0.026	0.023	0.0177	0. 0176	0.0160	0.0161	0.016
Dielectric constant, Mc									
1	3.9	4.15	4.05	4.05	5.05	3. 62	4.33	4.75	3.13
10	3.75	4.2	3.9	3.9	4.92	3. 53	4.4	4.63	3.18 (at 1 kc)
20	3.7	4.2	3.85	3.85	4.9	3. 5	4.35	4.60	3.91 (at 50 cps)
50	3.65	4.15	3.75	3.8	4.85	3.47	4.29	4.55	
100	3.6	4.03	3.7	3.75	4.8	3.44	4.25	4.51	3.2
Remarks	—	Best general characteristics	Best for high dielectric strengths	—	Highest thermal conductivity	Lowest coefficient of linear expansion			

* · 10^{-6} per °C; measured at 90 to 99°C for epoxy resins and at 69°C for polyster resins.

CHARACTERISTICS OF MICA-FILLED POLYMERS

Effects of Adding Mica to Most Polymers

The effects generally obtained by adding mica to a polymer are shown below. The degree of improvement depends very much on the polymer matrix and on the interface.

Property	Effect
Tensile strength	Increased or unchanged
Flexural strength	Increased
Flexural modulus	Much increased
Impact resistance	Decreased
Thermal expansion	Decreased
Dimension stability (shrinkage, warpage, crack resistance)	Much improved
Heat stability	Much improved
Thermal conductivity	Increased
Chemical resistance	Increased
Permeability to gases and liquids	Decreased
Stability to ultraviolet	Increased
Lubricity	Increased
Dielectric strength, resistivity	Much increased

The physical properties of mica-filled composites depend on:

- The polymeric matrix and matrix/mica interactions
- The volume fraction of mica
- The mean aspect ratio of mica *in the final composite*
- The mean flake size distribution of the mica
- Coupling efficiency between mica flakes and matrix
- Orientation effects

We will take these parameters, which are all interrelated in some way, in turn.

Polymeric Matrix and Matrix/Mica Interactions. As expected, the materials in the matrix contribute their physical characteristics in proportion to their volume fraction in the composite. Therefore, at equal mica content, a Nylon 66 composite will be stronger in flexure than a PP composite.

Other considerations apply. Certain polymers appear to function better with mica than others. These are PP, HDPE, PBT, PET, Nylon 66, TPX (*Tables 3* to *20*). Much less effect is seen in LDPE and ABS (*Table 8*). It appears that crystallinity favors the use of mica as filler. It is possible that mica acts as a nucleating agent and that a beneficial structure is developed.

Mica, like many fillers, may catalyse thermal decomposition of certain polymers (e.g., PP). Additional stabilizers are required for long-term thermal stability. Hindered phenolic and/or thio-dipropionate-ester antioxidants have been found to be effective.

The exotherm of thermosets (as epoxy, polyester and PU) is usually lowered by the presence of mica (19). When mica is used in thermosetting polyester, the cobalt promoter content is usually doubled, or additional amine promoter is used, in order to ensure proper curing.

To avoid side reactions with the isocyanate component, mica used in RRIM PU must be carefully dried and free from amine flotation reagents.

Volume Fraction of Mica. In general, increasing the volume fraction of mica enhances physical properties. At very high levels, processing difficulties are encountered. In thermoplastics, the temperature must be increased to obtain a processable melt viscosity, with the danger of degradation of the polymer. A high-melt-flow-index polymer is preferred, but the properties of such polymers themselves may be inferior. At high mica loadings, there may also be problems of removing entrapped air, of flake degradation due to the action of the screw on close-packed flakes, and poor orientation. For the same reasons, low-viscosity, thermosetting polyester resins are usually chosen. Defoaming agents (e.g., soya lecithin) are helpful in removing entrapped air. Some thixotropic additive, such as silica gel or ethylene glycol, may be used to prevent drainage on vertical surfaces when spraying-up polyester/mica mixes. Composites with mica volume fractions up to 50 percent have been injection-molded and up to 70 percent with thermosetting polymers, using special impregnated laminate techniques (3). Loadings of 20 to 30 percent by volume are more achievable in commercial single-screw and twin-screw extruders.

Aspect Ratio. If the aspect ratio is very high, the surface area tends to be high, also. A high surface area has a high demand for polymer; i.e., the viscosity, whether liquid or melt, is very high also. This creates processing difficulties. Composites using mica with aspect ratios of 300 or more have usually been made by special techniques. Aspect ratios between 30 and 120 are usually suitable for commercial processing techniques. Larger flakes with high-aspect ratios tend to be fragile and more easily degraded by the processing machinery. This effect is enhanced by higher-volume fractions.

Attempts should be made by using low-viscosity polymers and gentle processing methods in order to minimize flake breakdown. This usually manifests itself as fracture perpendicular to the plane of the flake rather than as cleavage.

Flake Size Distribution. It would seem, from theoretical considerations, that the reinforcing effects should depend on aspect ratio more than on flake diameter (3). However, large flakes create a rough surface texture on molded parts that may present sites for crack initiation, lowering the values of mechanical properties. Also, a rough texture is often not commercially acceptable. Very small flakes give a smooth, lighter-colored surface but are usually of low-aspect ratio and give lower flexural strength and modulus. However, impact resistance is improved. Very fine flakes tend to agglomerate and are difficult to feed into injection-molding machine. They are more difficult to disperse. In the case of near-spherical fillers and glass fibers, a range of particle-size distribution that is chosen to give close

Table 2. Comparative Properties of Spray-up/Lay-up Hybrid Sandwich Laminates Containing Mica as a Core and Commercial Lay-up All-Glass Laminates

Laminate #		8	9	10	11	12 (All Glass) Commercial	13 (All Glass) Commercial
Stacking Sequence		GC/GR/S_{60S}/GC/GR	GC, S_{60S}, S_{200S}/GR/S_{60S}/GC, S_{200S}/GR	GM/GR/S_{60S}/GM/GR	GM/GR/S_{60S} GM/GR	GM/GU/GM/GR (Various mats)	GM/GU/GR (Various mats and Rovings)
Reinforcement	Total	39.6	44.0	41.2	50.0	43.0	43.0
Content (Average)	Glass		15.4 GR	19.5 GR	19.2 GR	43.0	43.0
% by weight	Mica	12.4 GC 14.8 S_{60S}	13.0 GC 7.20 S_{60S} 8.40 S_{200S}	11.0 GM 10.7 S_{60S}	10.8 GM 20.0 S_{60S}	—	—
Flexural Modulus (Initial), psi · 10^{-6} (GN/m^2)		1.37 (9.45)	1.51 (10.4)	1.67 (11.5)	2.25 (15.5)	1.66 (11.4)	1.50 (10.3)
Flexural Strength, psi · 10^{-3} (MN/m^2)		35.9 (248)	34.3 (237)	34.4 (237)	50.5 (348)	44.2 (305)	37.7 (260)
Mode of Failure in Bending*		Tensile	Tensile	Tensile	Delamination	Tensile	Tensile
Unnotched Izod Impact Strength ft-lbs/in/(k/m^2)	Edgewise	—	—	—	60.2 (127)	67.1 (141)	89.6 (188)
	"Blow" on GR	36.6 (76.9)	29.8 (62.6)	29.6 (62.2)	—	—	—
	"Blow" opposite to GR	25.6 (53.8)	25.3 (53.2)	23.6 (49.6)	20.4 (42.9)	—	41.8 (87.9)
Specific Gravity		1.50	1.51	1.48	1.54	1.45	1.45
Specific Modulus, psi · 10^{-6} (GN/m^2)		0.91 (6.28)	1.00 (6.89)	1.13 (7.79)	1.46 (10.1)	1.14 (7.86)	1.03 (7.10)
Specific Strength, psi · 10^{-3} (MN/m^2)		23.9 (165)	22.7 (157)	23.2 (160)	32.8 (226)	30.5 (210)	26.0 (179)
Materials Cost, ¢/lb		43	43	45	44	56	56

* In bending, the load was applied on the first layer shown in the stacking sequence. Compressive damage was observed in all specimens; delamination was a secondary failure event except for #11.

Table 3. Dielectric Strength of Injection-Molded PBT* Composites Containing 30 w/o Suzorite® and Suzorex® Mica

Material	Dielectric strength,** Volts/mil.
PBT (Unfilled)	360
PBT/Suzorite® mica (60-S)	533
PBT/Suzorex® (60-PO)	558
PBT/Suzorite® mica (200-S)	528
PBT/Suzorex® (200-PO)	514

* Vituf 4716
** Testing conducting per ASTM D-149 (short time test, voltage increase at 500 volts/s.)

packing gives optimum mechanical properties in a composite. A repeat of John Milewski's work (20, 21), but using specially sized grades of mica, showed very little change in packed density regardless of whether the mica was closely sized or had a wide distribution of flake diameters, but with the same mean flake size.

In general, coarse-flake grades have a lower packed density than fine flakes.

Coupling Efficiency. To obtain good flexural strength in mica composites, it is important that the applied stresses be transferred from the matrix to the stronger flake. That is, there must be a strong bond between the matrix and the flake. Mica has a hydrophilic surface and is wetted well by polar polymers such as nylon, PBT, PET, epoxy, and thermoset polyester. Some improvement in mechanical properties of PBT and Nylon 66, such as tensile and flexural strength, of the order of 10-15 percent, is obtained with coupling agents (*Tables 7* and *18*).

Table 4. Thermoplastic Polyesters

	Polybutylene Terephthalate (PBT) (Valox® 310)		Polyethylene Terephthalate (PET) (Eastman 7352)	
	Virgin (unfilled)	40% Suzorite® mica 325 HK	Virgin (unfilled)	50% Suzorite® mica 60S
Tensile strength psi	7,280	9,900	10,400	11,500
Flexural strength psi	9,110	16,000	13,100	17,100
Flexural modulus psi	347,000	1,680,000	452,000	2,510,000
Izod impact resistance (ft.lb./in.)				
Unnotched 23°C	No break	3.1	7.3	1.9
−40°C	—	—	6.7	1.9
Notched 23°C	—	—	0.52	0.45
−40°C	—	—	0.52	0.45
Heat deflection temperature (°C at 264 psi)	53	169	80	218
Mold shrinkage, %				
Flow direction	2	0.6	—	—
Transverse direction	2	1	—	—
Dielectric strength Volts/mil	360	533 (558 with 60PO)	—	—

Table 5. Relative Warpage of PBT

	Mineral-filled nylon	30% Glass fiber reinforced PBT	GAFITE® LW (low-warp) PBT X7443R (mica-reinforced)
Warpage, not annealed, %	280	110	81
Warpage, annealed, %	380	160	110

Source: GAF.

Table 6. Physical Properties of PET Reinforced with Suzorite® Mica

	Unfilled Kodapak 7352	Kodapak® 7352 reinforced with 25% Suzorite® mica 60S	50% Suzorite® mica 60S	40% 60S 10% glass fibers
Tensile strength psi	10,400	10,600	11,500	11,740
Elongation at break, %	5	<5	<5	<5
Flexural strength psi	13,100	—	19,500	—
Flexural modulus psi ($\cdot 10^{-3}$)	452	1,220	2,510	2,740
Izod impact resistance				
Notched (23°C, ft.lb./in.)	0.52	0.50	0.44	1.8
(−40°C)	0.52	0.45	0.48	2.1
Unnotched (23°C)	7.3	2.3	1.9	—
(−40°C)	6.7	2.6	1.9	—
Heat deflection temp. (°C at 264 psi)	80	164	218	—
Specific gravity, g/cc.	1.38	1.59	1.85	1.82

Table 7. Effect of Silane Treatment on the Properties of Suzorite® and Suzorex® Mica/PBT* Injection-Molded Composites**

Property	30% Suzorite® mica (60-S) Untreated	30% Suzorex® mica (60-PO) Silane-treated	30% Suzorite® mica (200-S) Untreated	30% Suzorex® mica (200-PO)*** Silane-treated
Tensile strength, 10^3 psi	7.89	8.69	7.83	8.29
Flexural modulus, 10^6 psi	1.21	1.29	0.91	1.01
Flexural strength, 10^3 psi	12.8	14.6	12.6	14.5

* Vituf® 4716—Registered Trademark of Goodyear
** Composites prepared by direct molding of cryogenically ground PBT resin/Suzorite® mica dry blends. For large Suzorite® mica flakes, extruder precompounding yields normally lower results (see Technical Bulletin T-6) due to some flake degradation
*** Suzorex® mica 200 QX gives similar results.

Tensile and flexural strength of mica composites based on PP and HDPE are no better than can be obtained with talc, unless the bond is improved. This can be achieved by using a coupled polypropylene with an untreated mica or by using unmodified PP with a surface-treated mica, (9, 14). Both silane and nonsilane treatments have been found to be suitable (16).

Orientation Effects. Ideally, the mica flakes should be arranged so that they are in a plane, edge to edge, with the next layer superimposed, overlapping by 50 percent. When such an orientation is made, by special techniques, very high mechanical properties are achieved for the resulting composites. In injection-molded specimens, the flow orients the flakes parallel to the molded surface, but only near the surface. A random core exists in the center of the specimen. The thicker the section molded, the thicker this random core. The size of this core may be reduced in extruded sheets by increasing the length of the land of the die. Orientation improves when the extruded sheet is stretched or is otherwise deformed. In sprayed-up polyesters, the impact of atomised composite tends to

Table 8. ABS (GSM 4500 polymer) from Borg-Warner

	ABS 5% glass (long fiber)	ABS 10% Suzorite® mica 325 HK (92%-44μ)
Tensile strength psi	7,930	7,480
Flexural strength psi	10,300	11,000
Izod impact resistance Unnotched (ft.lb./in.)	5.8	4.1
Flexural modulus psi	437,000	619,000

Note that Suzorite® mica provides equivalent performance to that given by reinforcement with long glass fibers.

Table 9. Relative warpage of PET

Method—annealed disc 4 · 0.125 in.	
Rynite® RE 5060 (mica-reinforced PET)	5
Rynite® 530 (30% glass-fiber-reinforced PET)	110
Rynite® 545 (45% glass-reinforced PET)	125
30% glass-fiber-reinforced PBT	160
Minlon 10B (mineral-filled nylon)	5
Minlon 11C (mineral-filled nylon)	5

Source: New Engineering Plastics Resins based on polyethylene terephthalate, Richard A. Fleming, E. I. DuPont de Nemours Co., Inc.
Rynite® is a Registered Trademark of E. I. DuPont de Nemours Co., Inc.

Table 10. High-Impact Polystyrene (Resinex® SB625)

	Virgin (unfilled)	Reinforced with Suzorite® mica		
		200S (20%)	200S (40%)	60S (40%)
Tensile strength psi	3,030	2,820	3,090	2,940
Flexural strength psi	—	5,630	5,980	5,970
Flexural modulus psi	321,000	572,000	1,130,000	1,510,000
Izod impact resistance Unnotched (ft.lb.in.^{2})	18.2	4.38	2.10	1.57

Table 11. Water Vapor Transmission through PSt and PSt/Mica Films

Material	WVT,g.mm/m^2/24 hr. at 23°C
Polystyrene	1.67
Polystyrene + 37% by wt. Suzorite® mica 200-S	0.901

orient the flakes parallel to the mold. Rolling out the matrix by hand further improves this orientation.

PROCESSING CONDITIONS

Thermosets

Most work has been done with spray-up polyesters, although mica is commonly used as a filler for epoxy castings. Little success has been achieved when attempting to use mica in bulk molding compound (BMC) and sheet molding compound (SMC). In spray-up systems, mica can substitute for glass fibers, with some cost savings.

Thermosetting Polyesters. Composition. The usual choice is a polyester resin that is thixotroped with silica, either lightly or not at all. A viscosity range of 100 to 200 CP is preferred. The resin manufacturer is usually requested to incorporate double the amount of promoter that would be used for a glass-reinforced system. The catalyst (e.g., methyl ethyl ketone peroxide (MEKP)) is used at 0.75 to 1.00 percent. To help remove entrapped air, up to 1 p.h.r. of a defoamer, such as soya lecithin, may be added. Mica grades are usually −40 +100 mesh, or −100 +325 mesh (*Table 2*).

Hand Lay-Up. A mix with a 30 to 50 percent by weight of mica is used. This can be used as a paste to bond the outside shell to the inside shell of reinforced plastic (RP) boats, to bond transom skins, to fill the false keel, and as a stiffening layer on dinghy hulls and boat decks. Previously, short asbestos fibers had been used in many of these applications. It is usually trowelled on and rolled out by hand. The roller should be a short-haired mohair paint roller. A disc or grooved roller will tear up the surface.

Spray-up (22). Thirty percent by weight of mica in resin is usually the maximum tolerable because of viscosity. This mix may be sprayed by internal-mix spray equipment, modified to handle high viscosities and large flake fillers. Binks and Glas-Craft both have suitable modifications. Large nozzles, internal motionless mixers, and low-capacity, glass-fiber choppers are used. The sprayed-up laminates usually contain both glass fibers and mica. A blend of 20 percent mica and 15 percent glass fibers by weight has mechanical properties similar to that of a laminate containing 35 percent chopped-glass fibers.

End uses include boat decks, tub-shower units, swimming pools, and laboratory counter tops.

SMC and BMC. Mica may be substituted for part of the glass fibers. Mica has not found much use in these

Table 12. Injection-Molded Polypropylene Composites

	Polypropylene* 60%, filler 40% (except glass fibers 30%)						
	Unfilled PP*	Calcium** carbonate	Talc**	Wollastonite	Glass** fibers	Suzorite® 200HK untreated mica	Suzorex® 200NP treated mica
Tensile strength psi	4,930	2,770	4,270	4,470 (4,450)	6,340	4,050	6,190
Flexural strength psi	4,450	4,720	6,420	6,670 (8,320)	10,060	6,450	9,320
Flexural modulus psi (·10^{-3})	193	421	676	600 (535)	933	934	1,040
Izod Impact resistance Notched (ft.lb./in.)	0.45	0.75	0.45	— (0.9)	0.79	0.70	0.65
Heat deflection temperature (264 psi, °F)	136	183	162	— (178)	257	190	226
Coefficient of thermal expansion (23-73°C 10^{-5} in./in. °C)	7.4	5.3	4.0	—	2.0	—	3.3
Hardness, Durometer D	68	68	72	—	69	68	73
Mold shrinkage (% lengthwise)	2.0	1.4	1.2	—	0.3	0.8	0.8

* Profax® homopolymer 6523
** Commercial compounds
Figures in parentheses are Nyco data, otherwise data is as measured by Marietta Resources International.
Profax® is a Registered Trademark of Hercules, Inc.

Table 13. Polypropylene Homopolymer (Profax® 6523—Melt Flow Index 4)

	Virgin (unfilled)	Reinforced with Suzorex® mica	
		20% 200QX	40% 200QX
Tensile strength psi	4,750	5,470	6,760
Flexural strength psi	3,670	7,120	10,300
Flexural modulus psi	180,000	500,000	1,100,000
Heat deflection temperature (°C at 264 psi)	56	93	116
Izod impact resistance 23°C			
Unnotched (ft.lb./in.²)	No break	9.5	4.9
Notched, (ft.lb./in.)	0.45	0.59	0.49
Hardness, Shore D.	68	77	79
Mold shrinkage, %	2.0	—	0.8
Coefficient of thermal expansion, (73-163°F, per °F · 10^{-5})	7.4	—	3.3

Table 14. Extruded Sheets of Polypropylene Composites

	Polypropylene reinforced with		
	25% Calcium carbonate	40% Wood fibers	25% Suzorex® mica 200NP
Flexural strength psi			
Machine direction (m)	3,210	4,360	5,250
Cross direction (c)	2,850	3,820	5,080
Ratio m/c	1.12	1.14	1.03
Flexural modulus psi (· 10^{-3})			
Machine direction (m)	132	291	310
Cross direction (c)	130	209	295
Ratio m/c	1.01	1.40	1.05
Gardner impact strength in.lb. (0.6 lb. weight)	4.9	2.1	2.9
Specific gravity g./cc.	1.00	1.01	1.04
Void content %	7.1	—	4.2

compounds because of high viscosity and difficulty of incorporation.

Woodhams has invented SMC based on mica with powdered polyester resins (6).

Reinforced Reaction Injection-Molded Polyurethanes (RRIM PU). This appears to be a promising end use for mica. RRIM PU with mica can achieve a coefficient of thermal expansion equal to that of aluminum. Combinations of mica with glass fibers give the best physical properties (17, 18). Mica is added to the polyol component.

Thermoplastics

Most work on thermoplastics has been on injection-molded applications. Extruded sections tend to have rough surfaces.

Injection Molding. Powder Blending. If mica is mixed with pelletized polymer and is placed in a hopper, the mix segregates because of machine vibration and the first feed is too high in mica content. Mica blends (with powder, flake, or bead polymer) are stable. Blending should be low shear (i.e., drum tumbler or paddle mixer). High-speed devices, such as the Henschell mixer, are to be avoided. Dry blending is less costly than compounding. To ensure good mixing in the melted polymer, the screw should have a high L/D, and residence time should be relatively long. Fine mica flakes (e.g., 325 mesh) tend to segregate, to wet out poorly with the melted polymer, and are difficult to feed. A stuffer may be required. Where possible, the problem is avoided by the use of coarser flakes (−40 +100 mesh, −60 +125 mesh, and −100 +325 mesh). Fine mica flakes tend to produce a dusty environment. Feeding systems should be enclosed, as in the Color-

Table 15. High-Density Polyethylene Copolymer (Union Carbide 7914)

	Virgin (unfilled)	Reinforced with Suzorex® mica	
		20% 200NP	40% 200NP
Tensile strength psi	3,180	4,290	5,000
Flexural strength psi	2,070	3,750	5,850
Flexural modulus psi	123,000	330,000	670,000
Izod impact resistance			
Unnotched (ft.lb./in.²)			
22°C	No break	13.0	6.0
0°C	No break	11.0	5.4

Table 16.

	HDPE/PP Copolymer (UC DMDJ 7904) Reinforced with Suzorite® mica or other fillers (diluted to 10% and foamed VIA U.C. process)		
	Impact resistance Gardner, −30°F	HDT, 66psi	Mold shrinkage
Suzorite® mica 60S	77 in.lb.	62	13.8 mil/in
Talc	69	55	—
$CaCO_3$	65	56	—
Calidria asbestos	59	63	11 mil/in
Resin unfilled	73	55	16 mil/in

Table 17. High-Density Polyethylene/Polypropylene Copolymer

	HDPE/PP Copolymer (UC DMDJ 7904) Reinforced with Suzorite® mica		
	25% 200HK	25% 60S	40% 60S
Tensile strength psi	3,770	3,090	2,840
Flexural strength psi	3,920	3,520	4,120
Flexural modulus psi	388,000	428,000	816,000
Izod impact resistance Unnotched (ft.lb./in.²)			
22°C	8.6	8.8	3.4
0°C	7.1	6.3	3.0

Table 18. Nylon 66 (Zytel 101, Dupont)

	Virgin (unfilled)	Reinforced with 40% Suzorex® mica 325-PO
Tensile strength psi		
Dry	11,300	12,500
Wet (16 h water 50°C)	8,460	10,400
Flexural strength psi		
Dry	12,300	20,000
Wet	—	14,700
Flexural modulus psi		
Dry	443,000	1,360,000
Wet	126,000	840,000
Heat deflection temperature (°C at 264 psi)	67	201
Izod impact strength Notched (ft.lb./in.)		
Dry	0.80	0.53
Wet	—	0.93

tron CDE, to avoid contamination of molds and other compounds within the same shop.

Mica/Pellet Blends. Because of segregation, mica flakes and pellets must be metered separately. Colortronic, Inc. produces a metering/mixing/dispensing device that works very well with mica and with powdered or pelletised polymer (23).

Alternatively, the polymer may be fluxed alone and the mica metered into a downstream port. In this fashion, precompounding is avoided.

Machine Choice. Any horizontal injection-molding machine can handle these blends. The contact parts should be hardened. Mica is much softer than glass fibers and wollastonite, but is still much harder than polymer. A treatment that is suitable for talc-filled polymers is satisfactory—e.g., nitrided medium alloy-medium carbon steels, heat treated to hardness of Rc 50-63 (20a).

Molds. Hot-runner molds give excellent results, but cold runners work also. Sprues should be large and runners well-radiused at any bends.

Gates should not be smaller than the largest mica flake present, and should be as large as can be accepted, from a cosmetic point of view. Molds should be designed to avoid weld lines, which can exhibit tensile strengths 50 percent weaker than the bulk of the composite.

Temperatures. In order to get proper flow, all temperature settings must be increased. The amount depends on the polymer, mica type, and loading. Considerable experimentation is usually required. Rapid injection time is preferred. Too cold or too slow a shot

Table 19. Polyvinyl Chloride

	PVC + 10% Calcium carbonate	PVC + 10% Calcium carbonate + 33.3% Suzorex® mica 200-PO
Flexural strength psi	7,060	8,950
Flexural modulus psi	464,000	1,460,000
Coefficient of thermal expansion (0-60°C, °C · 10^{-5})	6.65	2.47

Note that the coefficient of expansion of the mica-reinforced PVC is the same as that of aluminum.

Table 20. Polymethylpentene (TPX®-Mitsui)

	Virgin	Reinforced with Suzorite® mica	Reinforced with Suzorex® mica	
		20% 200HK	20% 200NP	20% 200PO
Tensile strength psi	3,850	3,870	3,870	3,860
Flexural strength psi	3,820	4,540	5,100	4,860
Flexural modulus psi	179,000	331,000	402,000	362,000
Izod impact resistance				
Unnotched (ft.lb./in.²)	2.3	1.6	1.6	1.9
Notched (ft.lb./in.)	0.82	0.80	0.81	0.81
Gardner impact resistance (in.lb.)	4.1	—	4.1	—
Heat deflection temperature (°C at 264 psi)	47	51	65	65
Hardness, Shore D.				
23°C	75	80	80	80
120°C	45	50	47	50
Heat aging resistance (h at 150°C)	Passes 430	96	430	Passes 430

results in a frosty appearance, "mica splay." This may also be caused by overcooling the mold.

Extrusion. Similar considerations with respect to choice of polymer, polymer morphology, mica choice, and feeding methods apply to extrusion as to injection molding. Extrusion compounding of mica/polymer is often referred to avoid the dust problem in the molding shop, to ensure uniform color and mechanical properties, and to avoid feeding problems where a central polymer handling system is used.

Machine Choice. The choice of machine should ensure adequate mixing with little flake break down. In order of preference, best results are obtained with twin-screw, Transfermix, single-screw extruders. A Banbury mixer has been used with good results.

Blow Molding. Mica/HDPE is compounded conventionally and is used to blow-mold station wagon load floors, in the form of flat bottles with indented ribs that fuse together internally to form supports. Production tests of five-gallon "jerry cans" were not successful. During drop tests of the filled cans, they split at the knit-line. Some tool redesign could possibly overcome this. The low gasoline impermeability imparted to HDPE by mica would be advantageous.

Rotational Molding. Blends of HDPE powder and mica have been used experimentally to rotomold large tanks. The surface is not smooth enough unless the outer layer is rotomolded first with polymer alone.

ECONOMIC CONSIDERATIONS

Current Situation

In reviewing the economics of mica in plastics, a distinction between "fillers" and "reinforcements" must be made. Materials that have been added to plastic matrices to mainly increase bulk or reduce cost, without improving properties, are "fillers," and those materials that are primarily included to improve properties, and secondarily to reduce cost, are "reinforcements." Thus, mica is not a filler, but a reinforcement. It is a reinforcement that provides some specific property improvements, but is not of value when other properties are desired that mica cannot provide. Since the direction of plastic development will undoubtedly go in the direction of materials specifically tailored for an end use, or "engineered" plastics, this is of importance. Talc, calcium carbonate, glass fibers, carbon fibers, etc., are all materials that will be an important ingredient in the composites of the future, each supplying a desired feature. In some specific applications, mica is the material of choice. These applications include those where high flexural strength or modulus, good molding characteristics, freedom from warpage, and good heat distortion are important.

Talc and calcium carbonate are minerals that sell in the range of three to six cents a pound and provide certain selected properties at low cost. Glass fibers are particularly important for impact, tensile strength, and good overall performance, but cost 70¢ to more than $1.00-lb for them. Mica sells in the 8¢ to 12¢-lb range, untreated, or 20¢ to 30¢-lb with surface treatment and offers certain advantages at a notable savings over other reinforcements.

Either the end user, compounder, or resin supplier should design a system to best fulfill a specific end use and select the reinforcements separately or in combination that will achieve the required virtues. Mica, mica-talc, or mica-glass combinations are being established as important ingredients for engineered plastics.

Reinforced plastics have shown dramatic growth in the past 20 years, and recent econometrics suggest that this will be sustained. Kline, Reynolds, and Roussopolis, and SPI all agree on growth—the only variation has been predictions of scope and timing. If the use of all plastics in the U.S. and Canada grow from 20,000 tons/yr in 1979 to 50,000 tons/yr in 1999, it will be dramatic but no more dramatic than the growth from 1959 (3000 ton/yr) to 20,000 tons 20 years later.

These seers also predict a growth in reinforcements and fillers at a rate higher than that for plastics. These materials are forecast to grow from 3,000 tons/yr to more than 20,000 tons/yr between 1979 and 1999. The sales value of all resins averages $810/ton, or 40¢/lb, in 1979 and, by 1981, this had risen 20%; in 1980, polyethylene and polypropylene exceeded 45¢/lb, and the higher-priced resins—thermoplastic polyesters, nylons, etc.—were between 75¢ and $1.50/lb.

Current prices of reinforcing fillers in the 1980-82 period have, on the other hand, varied between 5¢ and $1.00/lb. These clearly have the ability to raise or lower the overall cost of the composite. It well behooves the designer to give careful scrutiny to the cost effectiveness of the reinforcing filler and the selected resin for an application. Sufficient variables exist to require computer programs carefully designed to tailor the required technical specification. Some resin producers are using this technique.

Consider two systems of similar tensile and flexural strength (*Table 12*)

1. 60% PP +40% Talc	Raw Material Cost 30.8¢/lb
2. 60% PP +40% Untreated Mica	Raw Material Cost 32.8¢/lb

For strength alone, the mica composite is the more costly. However, the composite also provides better dimensional stability, heat resistance, stiffness, and somewhat better impact resistance than the talc composite. These attributes may justify the additional cost. Also, the mica composite may not require precompounding, a costly process that is usually vital for a fine filler such as talc.

Again, consider the three systems

3. 70% PP +30% Glass fiber	Raw Material Cost 54.6¢/lb
4. 60% PP +40% Silane-treated mica	Raw Material Cost 40.8¢/lb
5. Mineral-filled nylon	Selling Price 120¢/lb

Essentially, these are equal in strength, stiffness, and impact resistance, but the fourth composite is lowest in cost, has least warping, and has the highest sur-

face hardness. If the highest heat resistance was needed, the third composite would be the choice. Clearly, end-use properties are the starting point, and suppliers of both resins and fillers should be qualified and available to offer a cost-effective formulation.

Reinforcing fillers each have a contribution to make to composite end-use properties, and each has a value (which is separately affected by purity, treatment, particle size, etc). Projected use of fillers in 1982 is 3MM tonnes as shown in Table 21 (24).

Kline, however, forecasts U.S. growth from 2.5 MM tonnes to 15.0 MM tonnes/yr, 1980 to 1985, or somewhat higher with a 40 percent annual growth rate.

Marietta Resources believes that the growth will be somewhat slower and will depend on market economic conditions and the ability of producers to provide sufficient technical know-how to justify compounders and molders to invest time and resources needed to obtain the desired technical results.

SUMMARY OF RECOMMENDATIONS

To obtain the best from mica/polymer composites, the following parameters should be observed:

Mica

- Aspect ratios 50-120
- Flake size 40 to 325 mesh
- Surface treated if necessary
- Volume fraction 10-50
- For improved impact resistance, use blends of mica with other fillers (e.g., calcium carbonate glass fibers, nylon or terephthalate fibers).

Polymer

- Crystalline to some degree
- Compatible with mica or surface treated mica
- Low liquid or melt viscosity.

Processing

- Low shear mixing in blends of mica/flake polymer, mica/polymer melt, mica/liquid polymer
- Control mica content by accurate metering devices
- Orient flakes by using thin sections for injection molding or extrusions, or by calendering or stretching.

Table 21. Projected Usage of Fillers in USA in 1981 and Current Selling Price

	M Metric Tons/ yr in USA 1985 Projection	1981 Selling price ¢/lb
Talc	300	5-15
Al_2O_3	300	10-120
Asbestos	450	15-60
Carbonates	1670	10-75
Cellulosics	105	—
Glass—Beads, Flakes	15	68-95
Silica	130	
Silicates (Incl. mica)	14	
	2984	

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DISCUSSION

L. A. Utracki: While preparing our manuscript on rheology of composites, we looked up some papers on economics of filler use in the plastics industry. In general, on the basis of material cost per volume, the use of even the least expensive filler—calcium carbonate—reduces material cost by a small margin. As far as mica is concerned, its price is comparable to that of polyolefins or even polystyrene. It is obvious that one has to justify the use of mica in these resins, not on the basis of material cost, but on performace. This situation

may change as the cost of feedstock increases. Could you comment on this?

M. Fenton: Any energy-intensive material, such as glass flake, glass fiber, or polymer, is going to increase in price at a rate roughly parallel to that for petrochemicals. On the other hand, the prices of natural minerals, such as mica, talc, and calcium carbonate, are going to rise less rapidly because their processing is not energy-intensive. As a result, future composites will tend to contain something like 20 to 30 percent mineral particles and 10 percent glass fibers to improve strength properties. I think we should direct our R/D efforts towards this sort of combination, which will be brought about by the high cost of glass fibers. Replacement of high-energy-content materials is likely to be widespread. For example, take the container industry. Dr. Woodhams mentioned the fact that mica reduces permeability to gasses when used as a reinforcing filler for high-density polyethylene. A plant to produce containers from mica-reinforced polymer is likely to be less costly than a steel can plant, which typically costs $600 million. The new technology, which will provide a substitute, will not only produce a cheaper raw material cost but will deal with the shortage of zinc, tin, and the high price of energy.

The other economic factor that I think is important is the property *vs.* material cost. If you pay 4¢ for calcium carbonate, 5¢ for talc, 8¢ for mica, 28¢ for coated mica, and 78¢ for fiberglass, what properties do you get with these and what is it worth to you? Does the surface finish really matter if the fenderliner is never going to be seen but has an adequate flexural strength and impact resistance? The grille-opening panel of an automobile has a multiplicity of bolt holes that must register with corresponding holes in subjacent parts so that they can be installed by a gang-bolting machine. If they do not mate, hand bolting must be used, at great cost. A compound that will allow machine assembly will fetch a high price. The next important characteristic is: how manageable will this new material be? What is going to be the rejection rate; how many parts can one make before die-wear is unacceptable? For example, if the new part will be 80¢ *vs.* $1.00 but there is a 50 percent failure because it does not mold properly, then you are better off staying with what you have. These are the reasons why development takes such a long time, especially in the automobile and appliance industries. These industries will not accept materials for replacement until all aspects are examined. They want performance, dependability (will it last over the lifetime of the car), and they want to know the effect on operating costs. When using a reinforced material that gives high abrasion on the extruder, the injection molding machine, or the coating equipment, it is important to know if the material will use 2 or 3 million dollars' worth of dies or molds in a year. Sometimes the cost saved on a material is negligible when compared to the extra cost of using it. These are the factors that one must think about when considering the economics of switching to reinforced plastics. Finally, it comes to the question of long-term economics. How is the cost/performance likely to change in the future? What will the ancillary costs be? These are the general lines of economic considerations, basic questions that we must ask ourselves, before committing to new composite systems.

R. E. Prud'homme. How do you do the silane treatment on the mica? Are you sure that the treatment is uniform? How do you check the uniformity of coating?

G. C. Hawley: That is a very good question. Most of the silanes are applied from solutions using some compatible solvent. Some of the methods are proprietary to Marietta. It is important to know how much silane has been deposited on the flakes. There are methods of doing it; one involves microscopy, with polarized light; TGA/DTA curves will often show characteristic peaks; Kjeldahl methods can be used for amino-functional silanes. However, there are two elements to consider: is the amount of silane correct, and is it keyed into the surface of the mica? The last element is probably the most difficult because, with DTA/TGA, you might find that silane is there in the correct quantity but, if it has oligomerized, it may not have established chemical bonds with the surface of the mica. The only satisfactory way of testing is to compound treated mica, mold some test bars, and measure the performance. If the physical characteristics are correct, then the silane is there in the right quantity and is doing its job properly. By this type of quality control, we have always been able to produce material that performs well. It is a rather slow method, but there are so many variables that are important that this is the only satisfactory way of getting the answer.

M. Fenton: I might add something to that. We are using two or three techniques, one of which is DTA/TGA, mentioned above. If the results are reproducible, and if they correlate with properties in the finished matrix prepared the same way every time, then we have some confidence that the same amount has been deposited. For other nonsilane coating systems, we use different techniques, such as burnout and wettability.

R. T. Woodhams: Dow Corning would like us to believe that silanes are the only thing that will give you good adhesion to an inorganic substrate, and they are probably right; there are very few things that will bond well to an inorganic substrate, and silanes have to be one of them. DuPont has for years used chromate complexes to improve bonding to glass. We have used iron complexes, and these are also very good. In the future, there will be many other substances other than silanes used to promote adhesion to inorganic fillers, such as mica. However, I think that there is too much attention focused on the silane-coupling agents. The adhesion is not the most important factor. My whole objective is to eliminate the silane because of its cost. We can put in a wax that is inexpensive, nontoxic, and can be added during the compounding (does not need to be added to the mica in a preliminary step, so it does not add to the cost). One can use 8¢/lb. mica and get the benefits of not only the coupling, which shows off by the improved tensile strength, modulus, and other mechanical properties, but also by faster and more complete dispersion, by less power in mixing. I mentioned one example with 5 percent but actually 0.5 percent is adequate: 0.5 to 1

percent of Chlorowax will effect a remarkable increase in properties, generally. Saul Newman from Ford invented that. I am sure that many others started immediately looking around to see why Chlorowax is so effective when silanes, which have been used for so many years, really did not contribute much in the way of property improvement. There are going to be many such surface treatments that are better than the silane and not as expensive.

G. C. Hawley: Some of the earlier work on mica with polypropylene was done using co-polymer, Profax PCO 72. This material has some coupling properties built in to the polymer, and it will give equally as good performance as silane treatment. The disadvantage is that there is a limited number of resins with a limited number of melt indexes and other properties. In order to be able to use any polymer at will, we went the other route. Also, at mica concentrations below 5 wt. %, it is a little cheaper. I am sure that there are many coupling systems that will be developed. Coupling agents are essential to the performance. If you take glass fibers and use them without the proper coupling system, you get poor results. The mica industry is going exactly the same way. The trend is to try to improve bonding by various surface treatments. We have to catch up to the degree of sophistication displayed by the glass fiber producers. One major defect of the chlorinated hydrocarbon system mentioned is that hydrogen chloride gas is produced when the compound is heated. This causes considerable corrosion of tooling, barrels, screws, etc. For this reason, it is not being used at the moment.

L. A. Utracki: In the preprints, you have a list of references that are internal references. Are these available?

G. C. Hawley: Yes, definitely, they can be obtained from Marietta Resources International, Ltd. If anybody wants a particular one, just write to the company, or to me.

L. A. Utracki: You mentioned that the polypropylene degrades in the presence of mica.

G. C. Hawley: Some of the muscovites are made by froth flotation using such agents as sulfuric acid, diesel oil, amines. None of these is particularly good for polypropylene. Taking a very white muscovite mica from U.S. sources and putting it in the polypropylene, one gets a very dark material; the polypropylene will start to degrade even during the injection-molding phase. However, even in the absence of these agents, degradation occurs. Silane-coupling agents increase degradation. A stabilizer "package" is used, as for talc, to overcome this problem.

L. A. Utracki: Why did you single out polypropylene? Is it not the same story for polyethylene?

G. C. Hawley: Very likely, but most of the work we did was of polypropylene. Due to its low density, availability, and low cost, it is one that has been singled out by the automotive industry. It is also a relatively simple system to work with. Linear low-density polyethylene will also be available in large quantities at a low cost in the near future and should be looked at, with mica as reinforcement.

D. Nercessian: Do you have any plans to reopen the research facility either here or in the States? In view of the tremendous new interest in mica and competition looking for mica applications in plastics, your position may not be so strong.

M. Fenton: We never lost our enthusiasm for continued research. We feel it is extremely important for our competitive position. Also, there are new resins coming along; there are many coating systems that should be evaluated, and I am sensitive to what Dr. Woodhams said about the effect of adding other materials that do not just improve the bonding. Yes, we do intend to expand, both here and in the U.S. I would like to comment on Dr. Woodhams' discussion about the effect of calendering, or reducing the thickness. This is most interesting. Our marketing partner in Japan has found that, having done just that to a sheet of polypropylene reinforced with mica, he obtained excellent acoustic properties. Some of the speakers that are being produced in Japan contain speaker cones of thermoformed Suzorite® mica-reinforced polypropylene. No one in North America is making this type of speaker. We hope to do some acoustic research to see what is really happening.

G. C. Hawley: I pointed out as long ago as 1977 that the ultra-high modulus of mica-reinforced composites would increase the velocity of sound therein and would enable speaker cones to be produced with a shallower angle whilst still keeping the sound waves in phase. Typically, I fear, the Japanese take suggestions like this and make them into commercial products, which we then buy from them.

Mechanical Properties of Mica-Reinforced Polypropylene Composites

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The influence of muscovite mica on the tensile, flexural, and mold shrinkage properties of composites with polypropylene (PP) were investigated. The best results in tensile and flexural properties at room temperature were observed for the physicochemical-treated mica followed by silane-treated mica. The mechanical properties could be correlated with the PP-mica interactions, as observed in the scanning electron microscope (SEM). In the present study, with mica aspect ratio equal to about 30, the optimum performance was obtained for the average flake diameter $80 \leq d\,(\mu m) \leq 280$. Finally, the results of coloration and weathering are discussed. It was found that the PP/30 percent mica formulation has superior weathering characteristics over the neat PP resin.

INTRODUCTION

There are three types of mica on the market listed in *Table 1*.

In Europe, muscovite is used as thermoplastic filler, whereas, in Canada, the main form of mica is phlogopite. The prime difference between these two is in color. The phlogopite is darker than muscovite and the biotite is still darker than phlogopite. In *Fig. 1*, the energy requirement at each stage of mica processing is shown. These data were provided by Micarec (1). Similarly, according to C. E. R. E. N. (2), the energy requirements for polypropylene (PP) and for compounding are, respectively, 84 MJ Kg^{-1} and 17 MJ Kg^{-1}. From these values, one can evaluate the energy requirement for PP with 30 percent mica as 76 MJ Kg^{-1}; i.e., an energy saving of 8 MJ Kg^{-1}, compared to pure PP.

There are a number of publications (3-9) that describe the method of preparation and properties of mica-reinforced PP. However, the type of mica used in these works is primarily phlogopite. Only in References 10-12 was muscovite used.

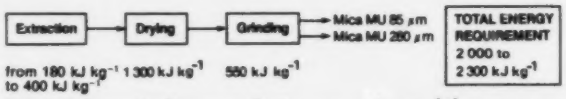

Fig. 1. Schematic diagram of mica processing and the energy requirements at each stage.

On the basis of the available information (3-12), we know that the following factors influence the mechanical properties of mica-reinforced PP:

- concentration of mica
- aspect ratio
- surface treatment
- processing
- size and size distribution of mica flakes

To optimize the mechanical performance, it is necessary to optimize simultaneously all these five parameters.

In the literature (8), there is an indication that high-aspect ratio improves the performance of the PP/mica system. However, from a practical point of view, the use of high-aspect ratio is difficult; during processing (extrusion and/or injection molding), the flakes break down in an irreproducible manner; the flake size and its distribution change. The interpretation of results

Table 1. Properties of Commercial Mica (15)

No.	Type	Chemical Analysis	Density	Hardness MOH's scale	Color
1	Muscovite	$K_2\,Al_4(Si_6\,Al_2O_{20})\,(OH,\,F)_4$	2.77-2.88	2.5-3	white
2	Phlogopite	$K_2\,(Mg,\,Fe^{+2})\,(Si_6Al_2O_{20})\,(OH,\,F)_4$	2.76-2.90	2-2.5	dark yellow or brown
3	Biotite	$K_2\,(Mg,\,Fe^{+2})_{0.4}\,(Fe^{+3},\,Al,\,Ti)_{0.2}\,(Si_{0.3}\,Al_{2.7}\,O_{20})\,(OH,\,F)_{4.2}$	2.7-3.3	2.5-4	black

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then becomes very difficult. For this reason, in the present study, we decided to restrict ourselves to the well-defined materials:

- unmodified PP
- muscovite mica with relatively low-aspect ratio of 30 in four different sizes

The main purpose of this work is to investigate the effect of flake size, concentration, surface treatment, and method of processing on the following properties: maximum tensile strength, Young's modulus, maximum flexural strength and modulus, shrinkage, fracture surface, and color.

EXPERIMENTAL

Mica

Muscovite mica, produced by Micarec and supplied by CMMP under the trade mark "MICA MU"®, was used. Four different batches differing in the average flake size were selected. Their characteristics are given in *Table 2*. In *Table 3*, the properties of muscovite are listed.

Polypropylene

The polymer was supplied by ATO Chimie, France, in the form of pellets. According to commercial information, the resin has the characteristic parameters, listed in *Table 4*.

Sample Preparation

The schematic of the sample preparation is given in *Fig. 2*. The schematic refers to the preparation of samples with surface-treated mica. In the case where no coupling agent was used, the process starts at the stage "Dry Mix I." The coupling agent was deposited using several techniques:

Table 2. Characteristics of Mica Samples

Code	Aspect Ratio	Size Distribution
Mu-20		
Mu-80	30	
Mu-280	30	50% > 50μ and 99.5% < 280μm
Mu-450	30	92% > 50μ and 99.5% < 450μm

Table 3. Muscovite Mica Properties

Maximum temperature (°C)	400-500
Tensile resistance (MPa)	250-300
Tensile modulus (GPa)	172
Diélectric constant	6-9
Resistivity (Ω.cm)	10^{15}

Table 4. Characteristic Parameters of Polypropylene Lacqtène P 3050 MN 1

Density (g cm^{-3})	0.90-0.91
Maximum temperature (°C)*	60-80
Tensile strength (MPa)	30-36
Tensile modulus (GPa)	1.1-1.4
Dielectric constant	2.2-2.3
Resistivity (Ω.cm)	10^{16}
Melt Index. (g /10 min.)	5
$\overline{M}_n$	10,000
$\overline{M}_w$	5,000-7,000

*of continous use.

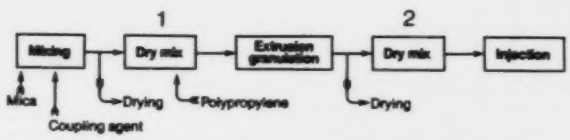

Fig. 2. Schematic diagram of mica/PP compounding process from raw materials to the tensile specimens.

- Slurry method was used with silane coupling agent only. Mica was placed in a low-speed ribbon mixer. The solution of a coupling agent in 95 percent methanol and 5 percent water was sprayed on mica while mixing. The amount of the coupling agents was calculated to give 1 (wt.%) coverage. After spraying, the slurry was heated to 80°C in order to dry the batch.
- To deposit the chloroparaffins, two different methods were used. For powdered chloroparaffin, the mica and the dry powder were blended in the ribbon mixer. With liquid chloroparaffin, the process started at "Dry Mix I" stage. The PP and liquid chloroparaffin were heated and mixed, then mica was introduced.
- In case of surface and thermally treated mica, the process started also at the stage "Dry Mix I."

The blend of mica and PP was granulated in a single-screw extruder (Samafor Bg 45) with L/D = 26, D = 45 mm and compression ratio 2:1. The temperature profile is shown in *Fig. 3*. Extruder strands of 4 mm diameter were quenched in a water trough and subsequently granulated. In the following stage, the grains were dried in an air-circulating oven at 100°C for 1.5 h, and subsequently injection-molded using 250 tons CREUSOT-LOIRE (SOMI 250-400) reciprocating-screw machine. The molded dog-bone-type specimens had the following dimensions:

thickness:	4 mm ± 0.4 mm
length:	150 mm
width:	10 mm ± 0.5 mm

Testing Methods

The specimens prepared as above were used directly as prepared or after aging. The aging conditions were as follows:

time	:	110, 1320, 3100 and 3600 h
temperature	:	38°C
humidity	:	50 percent HR
UV irradiation	:	Philips TL-0520 W

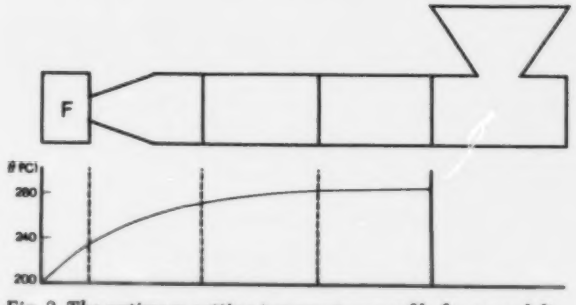

Fig. 3. The optimum setting temperature profile for a good dispersion of mica PP and output.

The ENSAM model was used. The wavelength of irradiation was between 300 and 450 nm and the power of the apparatus was $25 \cdot 10^{18}$ photon cm^{-2} h^{-1}.

The tensile strength and young's modulus were measured on an ADAMEL Lhomargy testing apparatus, according to AFNOR standard method number NFT 51-034 or ISO/R527 with the cross-head speed 50 mm min^{-1} at ambient temperature.

The flexural strength and modulus were measured on the same testing instrument using the flexural testing attachment. The procedure according to AFNOR No. NFT 51-001 or ISO 178 was followed: cross-head speed 5 mm min^{-1}, the distance between supports, D = 15 h where h = 4 mm is the sample thickness and at ambient temperature. The tensile and flexural tests values reported in *Figs. 5* to *12* are the averages of 10 separate measurements.

The shrinkage (in percent) reported in *Fig. 19* was calculated from the length of 48 h aged specimen and that of the mold cavity.

For the SEM observations, the specimens broken during the tensile test, as described above, were used. The samples were cut, metallized, and placed in SEM JEOL model T-200. The results are presented in *Figs. 13* to *18*.

RESULTS AND DISCUSSION

Injection Molding

First, the procedure of sample preparation had to be established, optimizing the injection-molding conditions: speed, packing time and pressure, nozzle and mold temperatures. It was found that, for each batch, the conditions stabilized only after 40 injections. For this reason, only the samples resulting from subsequent injections were tested.

The variation of the yield stress, σ, and the Young's modulus, E, for PP containing 30 percent of thermochemically treated mica with flake size of 80 μm as functions of packing pressure and time, mold and nozzle temperatures, is presented in *Fig. 4*. All the other injection parameters were kept constant. It was also found that the injection speed has an effect on the appearance but not on the mechanical properties; at higher speeds, the surface finish improves significantly.

On the basis of the data presented in *Fig. 4*, it is apparent that, for the best mechanical performance, the lowest values of the four processing parameters should be used. However, two observations should be made: the variation in σ and E, due to packing pressure and time, is relatively small, and these two parameters have less influence on the total injection-molding cycle; in order to shorten the cycle, both the nozzle and the mold temperatures should be held at minimum. It can be seen in *Fig. 4* that the nozzle temperature has the strongest effect on the σ and E. This probably can be explained by the flake orientation during the lower injection temperature; under these conditions, mica plays two roles—it reinforces and also serves as a nucleating agent. For these reasons, the following values of the processing parameters were used:

- high injection speed
- packing pressure of about 65 MPa
- packing time around 15 s
- nozzle temperature of 180°C
- mold temperature of 30°C

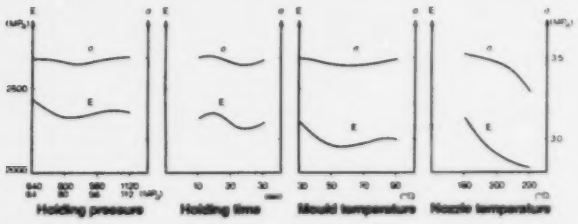

Fig. 4. Influence of the injection parameters on yield stress, σ, and tensile modulus, E.

Mechanical Properties

The influence of flake size and mica content on tensile and flexural properties is presented in *Figs. 5* to *8*. The symbols used are the following:

- PUR indicated virgin polypropylene
- 20, 30, and 40 represented the mica content in wt. %
- 20, 80, 280, and 450 μm represented the flake size

Figure 5 shows the influence of mica on yield stress. A decrease of yield stress with the amount of mica is observed. The effect is stronger for larger-diameter flakes.

One can see in *Fig. 6* that Young's modulus increases with the mica content; best results are obtained with flake size from 80 to 280 μm.

The maximum flexural stress, σ_f, (see *Fig. 7*) is obtained for 30 percent mica content with the flake size 80 μm. On the other hand, the optimum value for the flexural modulus, E_f, (see *Fig. 8*) is obtained using 40 percent of the same flakes.

One can observe from this figure that, for the flake size below 80 μm, the effect of particules on the reinforcement is less pronounced. The visual observations of the injection-molded specimens indicate that the untreated 20 μm-mica flakes have a tendency to agglomerate during the compounding process. This results in structural defects in the specimen and a decrease in me-

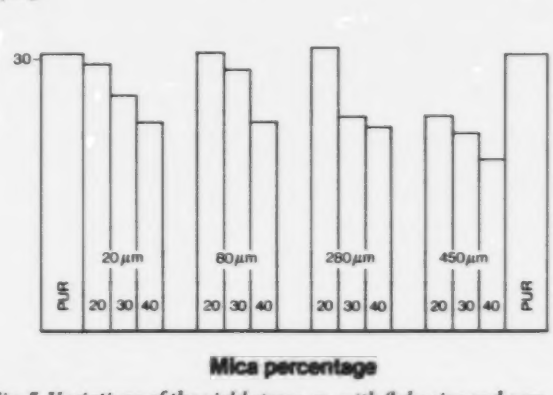

Fig. 5. Variations of the yield stress, σ_f, with flake size and composition for untreated mica/PP.

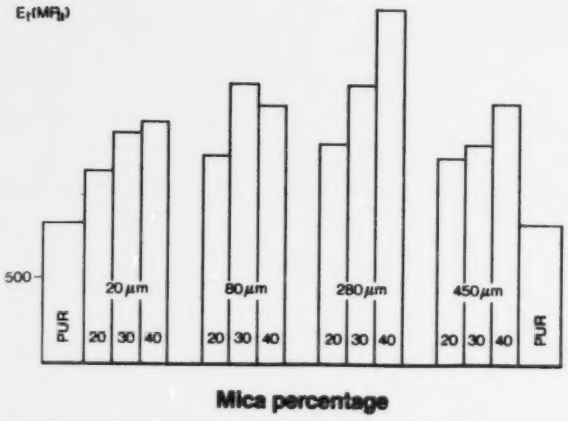

Fig. 6. Variations of Young's modulus, E_t, with flake size and composition for untreated mica/PP.

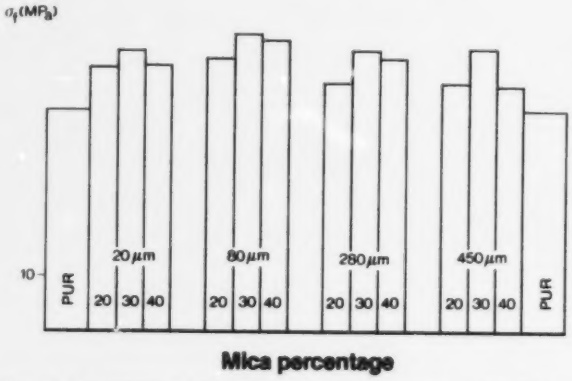

Fig. 7. Variations of maximum flexural stress, σ_f, with flake size and composition for untreated mica/PP.

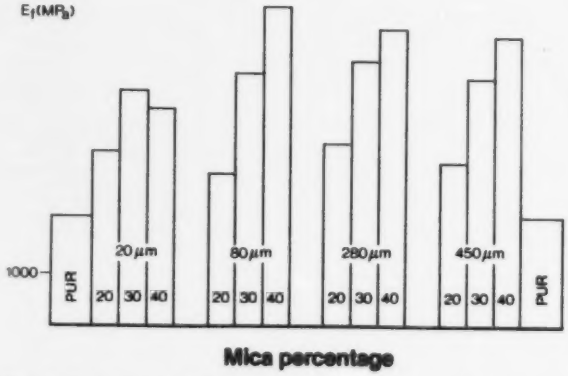

Fig. 8. Variations of the flexural modulus, E_f, with flake size and composition for untreated mica/PP.

chanical performance. We were unable to eliminate the agglomeration by variation of the technique used for the compounding.

The influence of surface treatment on tensile and flexural properties is presented in *Figs. 9* to *12*.

The symbols used are the following:

- 30 and 40 represented the mica content
- 80, 85, and 280 are the flake size
- P, MS, MC, and X represented the surface treatment as described in *Table 5*.

Table 5.

Symbol	Treatment	Product	Note
P	Physico-chemical	CMMP-Micarec	This is a pre-treated mica. Nature of the treatment is a proprietary information.
MS	Silane	A-174 (A-151 from Union Carbide	2 silanes have been tried, but only results with A-174 appear in this paper.
MC	Chloroparaffin	from Hoechst and I.C.I.	
X	Thermal	CMMP-Micarec calcined mica	

Example: 30 percent 80 P MS in the third column means: a Mica MU® with flake size of 80 μm treated physicochemically and with silane. The results obtained for the filled PP are always compared with neat PP. From the yield stress and modulus data on *Figs. 9* and *10*, one can see that 30 percent 80 P MS gives best results. The samples 30 and 40 percent 80 P, which contain physicochemically treated mica, also show quite a good performance. It seems very important to note that

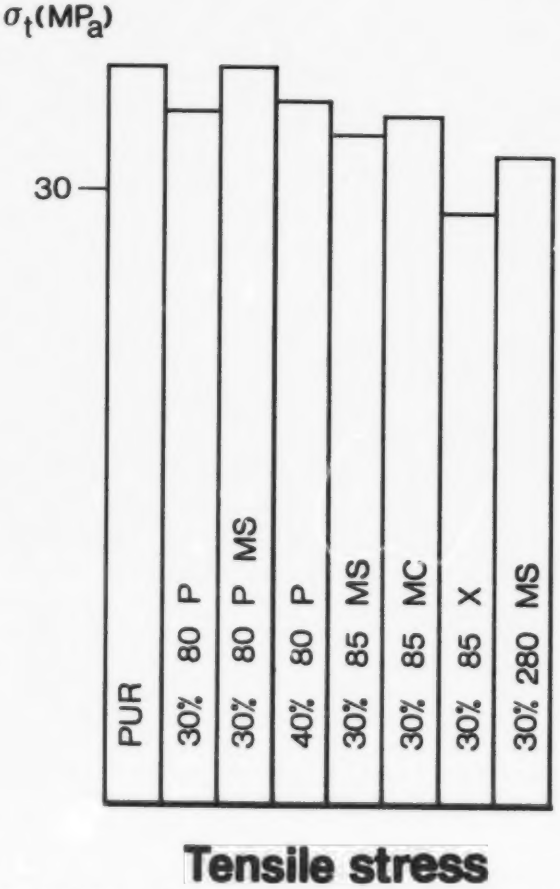

Fig. 9. Influence of different mica treatments on the yield stress, σ_t, for mica/PP composites.

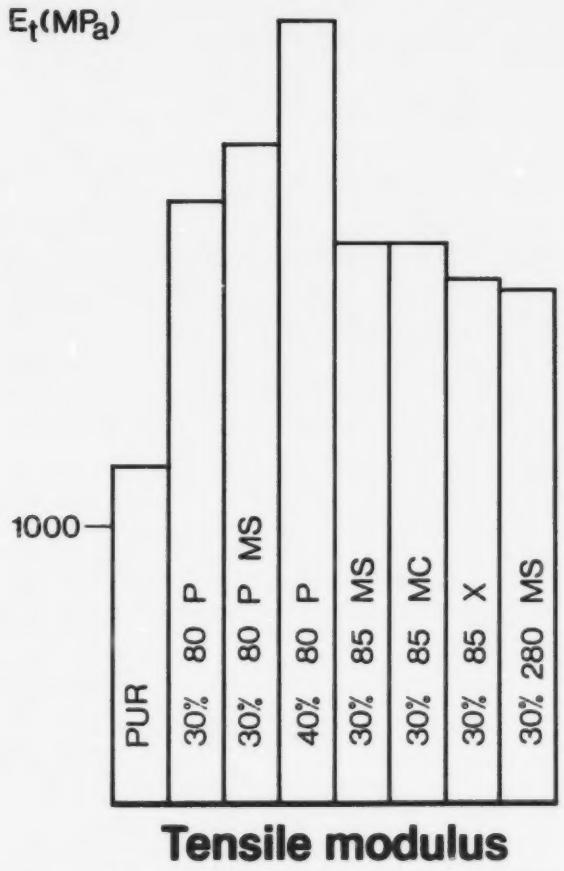

Fig. 10. Influence of different mica treatments on the Young's modulus, E_t, of mica/PP composites.

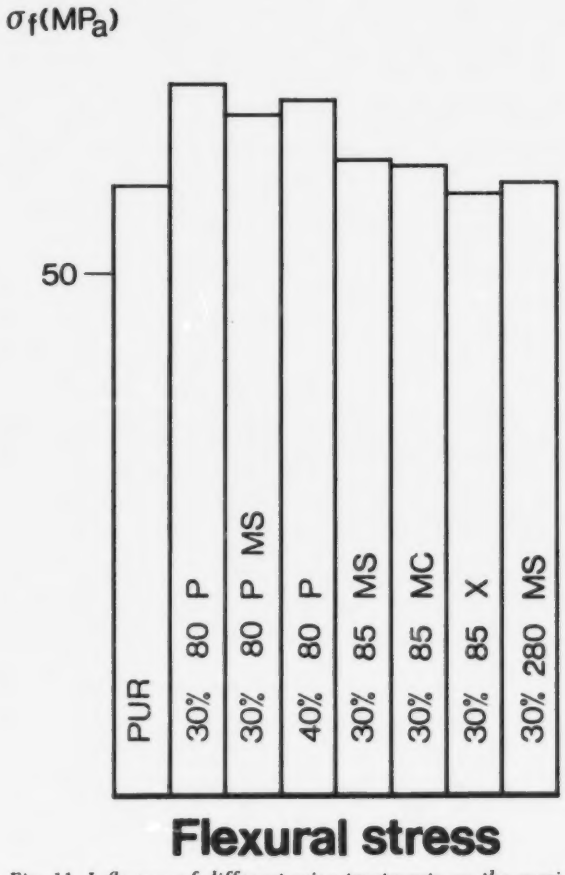

Fig. 11. Influence of different mica treatments on the maximum flexural stress, σ_f, for mica/PP composites.

the composite with 40 percent mica 80 P has better tensile stress and modulus than the composite with 30 percent; as the data in *Figs. 5* and *6* indicate, the opposite effect was noted for untreated mica.

These results demonstrate the importance of the interaction between polypropylene and mica for good mechanical performance. Coating mica with silane and chloroparaffin gave about the same results. However, chloroparaffin caused discoloration of the materials from brown to black and should not be used in formulations where color is important. Looking at the flexural stress data in *Figs. 7* and *11*, we can see that, in both cases, σ decreases slightly with mica content (from 30 to 40 percent) while, at the same time, the magnitude of σ_f increased by 26 percent for the sample containing physicochemical-treated mica. Comparing results presented in *Figs. 8* and *12*, one can see the influence of surface treatment on the flexural modulus. Here again, the physicochemical treatment of 80 μm-flake-size mica offers the best performance. In summary, it seems that the best method of improving the flexural properties is, indeed, the physicochemical treatment.

SEM of the Fractured Surface

The maximum flake bonding occurs for the physicochemical and silane treatment seen in *Figs. 17* and *18*. It seems that there is more bonding on the edges of flakes (viz. *Fig. 17*), which may be explained by two mechanisms: the edges are more porous (i.e., the penetration of PP macromolecules and the resulting mechanical bonding is more likely and, for the same reason, the chemical treatment must preferentially affect the edges and generate a better mica/PP interaction around this zone. The scanning electron microscope (SEM) was used to observe variations in PP-mica bonding resulting from the surface treatment of the filler. In *Figs. 13* to *18*, the SEM micrographs of the fractured surfaces are presented. In all cases, the samples containing 30 percent treated mica were fractured using the tensile tester. The following treatments were used:

in: *Figs. 13* and *14*	chloroparaffin
Fig. 15	silane
Fig. 16	physicochemically
Figs. 17 and *18*	physicochemically and silane

Examination of these photomicrographs reveals two types of fracture: in *Figs. 14* and *16*, the brittle fracture prevails while, in the other cases, the ductile fracture is more pronounced. It should be noted that, in all the fractured surfaces, both mechanisms are present to some extent. For the samples with better bonding (i.e., a more effective surface treatment), the ductile mechanism is the predominant.

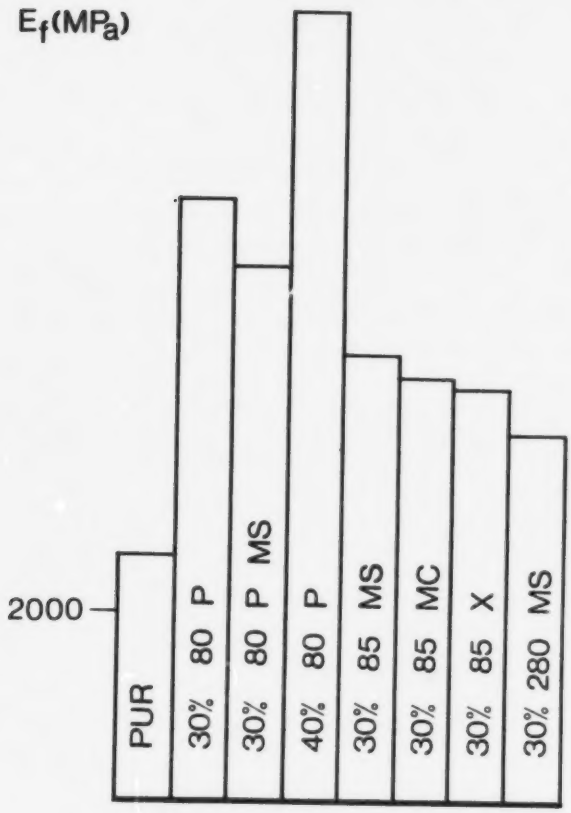

Fig. 12. Influence of different mica treatments on the flexural modulus, E_f, for mica/PP composites.

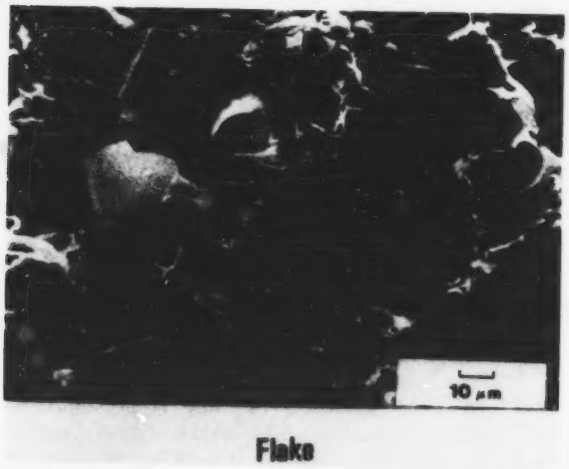

Fig. 13. Fractured surface of the 30% MU® 80 MC specimen in a ductile mode.

In *Fig. 19*, the relation between the amount of shrinkage and mica content and the flake size is shown. For 40 percent of mica, the same amount of shrinkage for flakes of 80, 280, and 450 μm is observed. A slightly larger shrinkage is observed for the smallest 20 μm flakes. This difference can be explained by the fact that, for small flakes, we were unable to obtain good dispersion. When the mica content is reduced, variations in shrinkage also become dependent on flake size and orientation. With the dog-bone specimens, it was

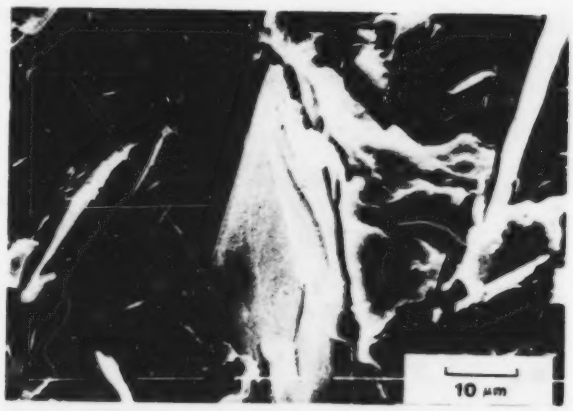

Fig. 14. Fractured surface of the 30% MU® 80 MC specimen in a brittle mode.

Fig. 15. Fractured surface of the 30% MU® 85 MS specimen.

Fig. 16. Fractured surface of the 30% MU® 80 P specimen.

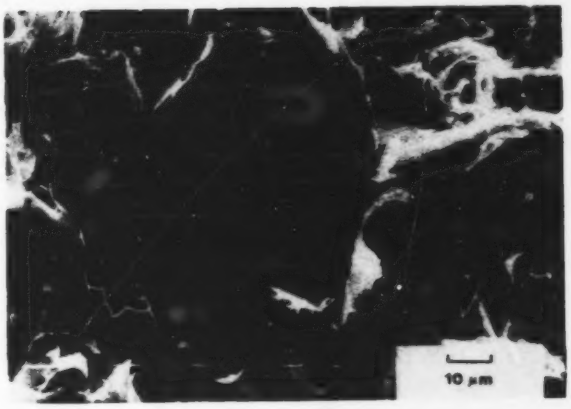

Fig. 17. Fractured surface of the 30% MU® 80 P MS specimen.

Fig. 18. Fractured surface of the 30% MU® 80 P MS specimen.

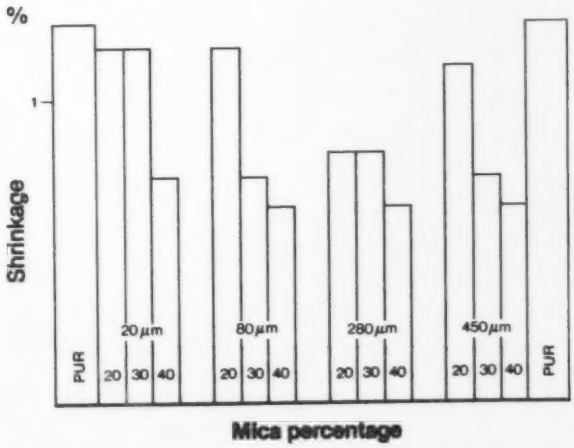

Fig. 19. Variations of the amount of shrinkage with flake size and composition for untreated mica with PP.

very difficult to estimate the shrinkage in the transverse direction. However, it has been reported (4) that PP reinforced by mica shows a reduction in shrinkage in both directions.

Using color preblends, the dyeability of neat PP and PP-mica blends was evaluated. It was found that, using the same amount of white and yellow pigments, a good coloration was obtained for both PP and PP-mica composition.

Figures 20 and *21* present the results of aging tests for polypropylene and its mixtures with 30 wt % of physicochemically treated mica with flake size 80 μm and mica 85 T. From the untreated mica 85 (with flake size of 85 μm), the fines were removed prior to blending to obtain what we call mica 85 T.

In *Fig. 20*, the dependence of tensile stress on aging time is shown. It can be seen that, after 1000 h, the composites perform better than polypropylene. In particular, the sample containing the physicochemically treated mica 80 P shows a superior behavior over that containing the untreated mica 85 T. The difference between these two materials became greater with the time.

Figure 21 refers to the reduction in yield stress defined as $100\,[\sigma_y(t=0) - \sigma_y(t)]/\sigma_y(t=0)$, where t is the aging time. One can see that mica is an effective

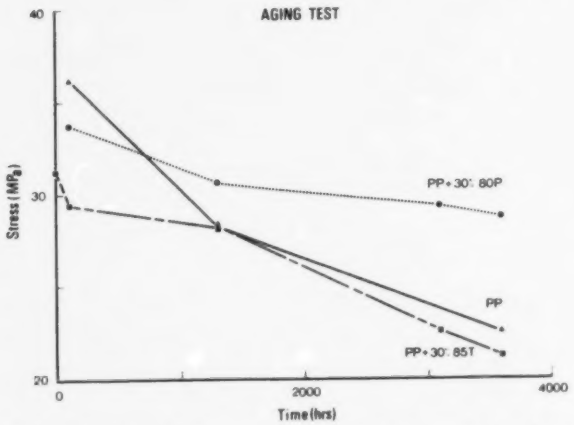

Fig. 20. Influence of aging time on the yield stress for three types of material: Neat PP, untreated PP, and physicochemically treated mica/PP composites.

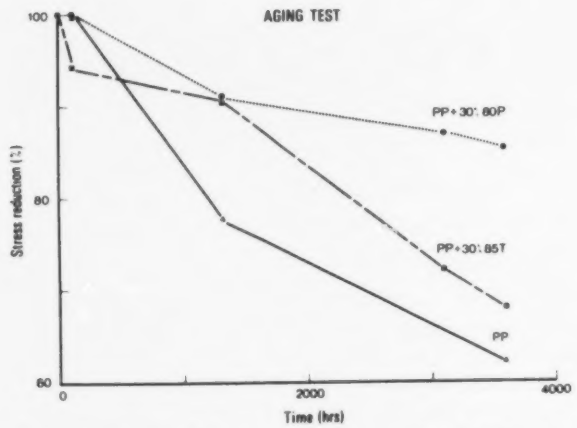

Fig. 21. Reduction of the yield stress vs. aging time for PP and its mixtures with untreated and physicochemically treated mica.

agent to improve UV stability of polypropylene. This indicates that mica-reinforced polypropylene can be successfully used for outdoor applications.

CONCLUSIONS

Muscovite mica improves the mechanical properties of polypropylene. However, one should pay attention to the flake size and distribution, surface treatment, and compounding process in order to optimize the performance. Muscovite mica offers a better possibility of pigmentation; this may be important for several applications. It was shown that PP/muscovite has increased UV stability. Similarly, one can expect that electrical or chemical properties of PP can be improved by the addition of mica. The total energy consumption, including polymerization of propylene, compounding and processing, was found to be less for the composites than for neat PP resin.

ACKNOWLEDGMENTS

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DISCUSSION

H. Fenton. What is this physicochemical treatment that you talked about? Is this different from silane or other treatments?

B. Sanschagrin. Physicochemical treatment is proprietary information. All I know is that this is a thermal treatment followed by chemical treatment.

G. C. Hawley. What is possibly happening here is that certain micas expand on heating. This has been noted for muscovites and some phlogopites. The process was developed for the paper industry and it involves heating the mica. This opens up the layers, then the acid infiltrates between the layers. Passing it through a bath of a base generates CO_2 between the layers and finishes the delamination. The treatment usually results in a very high aspect ratio. I am surprised that yours is only about 30. In most cases, for an efficient mica paper production, you need something around 200 or 300.

B. Sanschagrin. The physicochemically treated mica, which I used, was crushed and screened after treatment to generate uniform particles of about 80 μm. Probably the crushing resulted in lowering of the aspect ratio.

L. A. Utracki. The price of the physicochemically treated mica is about 25 percent higher than that of the untreated mica. However, I presume that the treatment clears the surface of the flakes from diesel oil and other floating agents that usually hinder the binding.

G. C. Hawley. Yes, I think this is an extremely important facet. The action of acid would tend to neutralize amines that are present on the surface. The process has two functions: delamination and cleaning of the surface. In addition, during the wet stage of the process, the fine particles of mica tend to float off what gives larger and more uniform flakes. Your micrographs show very close sizing.

R. T. Woodhams. I am curious about the type of mold used to make tensile bars. We found in our studies that, if we used pin gates, the results were very poor. Gradually, we kept enlarging the gates into the mold. This probably was associated with jetting as the material enters the cavity. With the valve-gated mold and heated runner system, we were able to get a much larger tensile strength. It is possible to get much higher tensile strength if you open up the gates considerably. I am not too sure what that does to the flow, but it has a profound effect on the resulting strength of the parts.

B. Sanschagrin. We used a cold runner system with a large gate. The gate was rectangular, 20 · 1 mm. We injected from the end of the specimen, which was 4 mm in height. We did not observe the mold shrinkage at the calibrated section of the tensile bar, which would be a sign of poor gating.

L. P. Blanchard. Would it not be better to mill instead of molding the specimens? When you injection-mold the sample, you have all sorts of problems related to the flow, reformation, etc., whereas press molding a plate from which you can cut out the specimens can be more easily controlled.

B. Sanschagrin. Our goal was to evaluate the mica composites molded under conditions similar to those used in industrial practice. On the other hand, if (as you sug-

gest) we would prepare samples by pressing and milling or stamping, then the important effects (e.g., skin/core structure and flake orientation) would be neglected. The results would probably look better, but they would be of no value to the industry.

L. A. Utracki. It is true that changing the injection-molding parameters over also changes the performance of the molded specimens. It is also true that one can get better reproducibility of data using other methods of sample preparation. However, Sanschagrin's conclusions are not only valid because of their industrial applicability, but also because (a) the differences of sample performance on which the conclusions are based are larger than the standard deviation, and (b) the relative magnitude of the averaged data should be independent of the processing conditions.

B. Sanschagrin. The sequence of the test data, the relative order of the specimens, will not be affected by changes in the molding parameters, even if the magnitude of the arranged results will change.

Industrial Applications and Properties of Short Glass Fiber-Reinforced Plastics

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Short glass fibers for reinforcement of plastics have been commercially produced for over three decades. During this period, they have been used in virtually every polymer, as well as in other matrices, such as concrete and plaster. Their tensile strength/cost performance is still three times that of Kevlar® and more than 30 times better than carbon fibers. Similarly, excellent modulus/cost performance and high temperature/cost performance can be achieved. This article gives a review of short-fiber composites: their properties and use. Included is a comparison of compounding *vs.* in-house blending, fiber/flake hybrids, and reinforced polymer blends. Finally, several new materials still in development stages will be examined.

INTRODUCTION

First commercial glass fiber manufacturing facilities were established in the thirties. Technological advances in glass fiber manufacturing technology enabled production of diversified, inexpensive raw materials described by Lowenstein (1) and Mohr, *et al.* (2).

Short-glass-fiber-reinforced polymers (SFRP) use reinforcing fibers, usually in a chopped strand form, from 3 to 12 mm long. Other forms of fibrous reinforcements are rovings, chopped strand mat, and milled fibers. Naturally occurring fibers such as Fybex, a fibrous potassium titanate mineral, and asbestos fibers can be used in plastic composites, but give mediocre performances (3, 4). Advanced fibers (boron, aluminum, carbon, and aramid) are predominantly used in a continuous form. However, medium modulus graphite fibers are available in thermoplastic molding compounds, as reported by Theberge, *et al.* (5).

It is important to note that composites containing short glass fibers in matrices other than plastics represent large and faster-growing markets for glass fibers. Major matrices are gypsum for wallboard, concrete for building panels, and asphalt for shingles.

A summary of the major molding processes that may utilize SFRP is presented in *Table 1*. Injection molding is the most common process, due primarily to the economic advantages in large-scale production and proven complex shape technology. Although this paper has been directed towards injection molding, some specific economic aspects are examined for other processes.

The second section, on materials, is primarily focused on glass fibers. Injection molding materials and applications are discussed in the third section. Other major molding processes for SFRP (Thermoforming, Stamping, and RRIM) are covered in the fourth section. In the final section, future trends are discussed.

All materials property data reported have been generated at the Textiles and Reinforcements Development Center of Fiberglas Canada Inc., Guelph, Ontario.

MATERIALS

Part performance/cost can be maximized only through detailed analysis of the interdependence between materials, processes, and design criteria. Economics of SFRP are predominantly dictated by material cost/performance.

Glass Fibers

Typical chopped strand contains 800 filaments, most commonly of 13-μm diameter. The strand is impregnated with a sizing system compatible with the end-use polymer.

The sizing system may contain film formers (adhesives), coupling agents (usually silanes), lubricants (fatty acid amines), antistats (simple or quaternary salts), wetting agents, and other specific property modifiers. Detailed description of sizing technology is given by Lowenstein (1). The size system is the most important variable affecting performance of short-glass-fiber-reinforced plastic, as recognized by most investigators from Plueddemann (6) and Marsden (7) to Temple, *et al.* (8).

In spite of the complexity of sizing systems, the role of silane coupling agents has received almost exclusive attention and has dominated the interface sections of the SPI RP/C conferences. Although Fourier transform

Table 1. Major Molding Processes for Short Glass Fiber Reinforced Composites, Materials and Applications

Molding Process	Major Resins	SFRP Material	Applications
Injection Molding	Polypropylene Polystyrene ABS Nylon Polyester Polycarbonate	—RTP compound a) Long glass b) Short glass —Dry blend —BMC	At least 80 different car components (steering column housing, oil pan, bumper bar, under the hood parts), tool handles, cases and gears, electrical components.
Compression and/or transfer molding	Unsaturated Polyesters	—BMC	Automotive (spoiler extenders, ducts, heater housings), circuit breakers, appliances (bases, cases), microwave cookware.
Thermoforming	HDPE, Polypropylene	—Sheet	Containers, housings, large industrial parts.
Stamping	Polypropylene	—Sheet	Seat shells, containers, fender liners, car fascia, boxes, car battery trays.
RRIM	Urethane	—In situ polymerized Resin + glass	Fenders and other automotive panels.
Structural Foam	Polyethylene Polycarbonate PVC, ABS, Nylon	—RTP pellets + blowing agent	Business machine housings, internal frames, transport tops, seating.
Rotational Molding	Polyethylene Polycarbonate	—Resin (powder) + glass	Stress free hollow shapes.

infrared spectroscopy, employed by Koenig, *et al.* (9), offers analytical proof that a reaction between aminosilanes and epoxy matrix may occur, no such analytical evidence exists for thermoplastics. In order to explain the performance data with silanes, many theories have been proposed: covalent bonding (thermoset), weak hydrogen bonding, polar attraction (polar thermoplastics), interpenetrating networks (polyolefins), etc.

Whatever the outcome of the great coupling debate, silanes do improve the wet out of glass fibers by the polymer matrix, thus ensuring excellent interface. They also remove water from the glass surface by either reacting with it to form silanols or by a chemical adsorption mechanism (glass fibers break mainly because of water corrosion crack propagation).

The effects of other-size ingredients have not been well-documented. A factorial experiment on chopped-strand sizes for polypropylene reinforcement, carried out by Santrach (10), indicates a strong dependance of heat deflection temperature (HDT) and tensile strength on variables other than coupling agents. The most important factors were the amount and the type of film former and the type of lubricant. Kardos, *et al.* (11), proposed a complete ductile innerlayer for monofilament fibers.

Injection Molding Materials

There are two basic ways of molding reinforced plastic parts:

- Materials are fed directly into injection-molding machine as a dry blend.
- Pre-compounded pellets are used.

Dry blending of chopped glass and polymer is a widely used technique, especially where large production volumes of parts offer a distinct economic advantage over pre-compounded pellets (12). Normally only powder resins or smaller-particle-size polymers are used due to dispersion limitations in present injection-molding machines.

Most pre-compounded pellets are produced on a single-screw extruder and contain well-dispersed short fibers (mean fiber length is 0.2 to 0.7 mm) (13). Long fiber compounds are, however, produced in a coating operation where fibers are as long as a pellet (typically, 9 mm) but nondispersed in the polymer. Advantages of well-dispersed compound are discussed by Cloud, *et al.* (14).

INJECTION MOLDING

Reinforced vs. Neat Polymers

The benefits of fibrous reinforcement were recognized early. A summary of these advantages is given in *Table 2*.

Polymer Matrix Effects on Physical Properties

Goettler and his coworkers (15) recognized improved glass fiber wetting with engineering resins. Thus, for the 30 percent w/w of glass fibers, the compound tensile strength with nylon 6/6 is increased more than with polypropylene (97.5 MPa increase vs. 33 MPa) (16). Based on the original strengths, this is, however, a 220 percent and a 197 percent increase, respectively. In general, if the property enhancement is expressed in terms of percentage increase over base polymer, polyolefins perform better.

Emmett (17) observed that, with the addition of glass fibers, HDT can be increased to near the melt point of crystalline resins, but only to the glass transition temperature of amorphous resins.

Table 2. Advantages of Glass Fiber Reinforcement

1. Higher modulus
2. Higher strength
3. Superior heat resistance
4. High impact (brittle polymers)
5. Creep resistance
6. Lower cost/performance
7. Resin (energy) conservation
8. Surface hardness increase
9. Reduced thermal expansion
10. Reduced shrinkage
11. Part consolidation

Reinforced Polypropylene

High-temperature performance, good physical properties, and low cost have been the main reasons for the penetration of reinforced polypropylene into the automotive market. Reinforcement allows replacement of costly engineering resins with polypropylene or use of the wide-spec, reground materials. Mechanical properties of 20 percent glass-reinforced polypropylene are compared to nylon 6/6 in *Table 3*. Data on reinforced wide-spec polypropylene are also included for comparison with prime grade resin.

Major reinforced polypropylene markets continue to be in the automotive applications, such as: under-the-hood parts (fan shrouds, etc.), heater and air conditioner ducts, lamp housings, and fender liners. Other applications include bases and housings for appliances and ABS (acrylonitrile-butadiene-styrene terpolymer) replacement. A good review of reinforced polypropylene performance and applications is given by Wenger (18).

DRY-BLEND VS. PRECOMPOUNDED PELLETS

Economic advantages of the dry-blend system have been recognized for over a decade. Introduction of new powder resins helped a tremendous growth of this system in the automotive industry. It must be pointed out, however, that an improvement in injection-molding machinery is also required before this system reaches its full potential. Some of the major advantages of both systems are listed below.

Pre-Compounded Material Advantages

- Short-fiber compound may have a more uniform glass content, reducing variance from part to part.
- Shear work, and therefore wear, takes place in the compounding screw rather than in the injection-molding machine.
- Smoother part surface may be achieved due to better glass-fiber dispersion.
- Compound supplier is responsible for engineering data, materials performance, and quality.
- Compounder may develop specialized formulations to meet specific requirements.
- Compounded material is supplied in a predried pellet form, which results in easier handling.

Dry-Blending Advantages

- Material cost savings.
- Energy conservation in dry blending over compounding.
- Higher mechanical properties due to longer fiber length in the part. This is especially true for impact strength.
- Flexibility in use of reinforcing materials, additives, and regrind.

Processing variables have a major effect on final properties of injection-molded parts of either dry-blended or precompounded SFRP. Processing conditions are usually recommended by the compounder (e.g., Theberge (19)) or by the resin supplier, in the case of dry-blending (e.g., Egbers (20)), who find a strong dependance of notched-izod impact strength on injection factors. The most significant factors are: screw speed, gate size, back pressure, melt temperature, and mold temperature. This is in agreement with previous studies by Moskal (21) and Darlington (22). Glass-fiber-length degradation in injection molding of dry blended and compounded materials was investigated by Schweizer (23). He found that, for precompounds, most of the damage occurs in the extrusion compounding and in the injection unit barrel. No further fiber attrition occurred in the sprue, runners, and gates. When molding dry blends however, fibers were damaged further in runners and gates. This is due to the longer fibers in dry blends, experiencing wall effects in runners and gates.

Mechanical property data for 20 percent glass-reinforced coupled polypropylene and styrene maleic

Table 3. Mechanical Property Comparisons: Prime Grade Versus Reinforced Wide-Spec Polypropylene and Reinforced Polypropylene Versus Nylon 6/6

Property	ASTM Method	Units	Prime Grade Homo Polypropylene	20% Glass Reinf'd Wide-Spec Polypropylene	20% Glass Reinf'd Prime Polypropylene	Molding Grade Nylon 6/6
Tensile Strength	D638	MPa	31.0	34.0	48.1	81.3
Tensile Modulus	D638	GPa	—	4.9	5.0	2.7
Elongation	D638	%	>200	2.2	2.64	80
Flexural Strength	D790	MPa	48.0	57.2	77.8	103
HDT at 264 psi	D648	°C	49	105	138	65
Izod Impact Notched	D256	J/m	21.4	48.0	64.1	48.0
Izod Impact Unnotched	D256	J/m	—	267	293	—
Specific Gravity	D792		0.91	1.05	1.05	1.14
Relative Cost/Vol.	N/A		1	0.92	1.4	5.0

NOTE: Cost data based on 1980 figures.

anhydride copolymer indicate better overall properties for dry-blended compared to precompounded materials, as shown in *Table 4*.

HYBRID REINFORCEMENTS

Theberge (24) and Cloud (25) have reported on mechanical property data for carbon and carbon/glass-reinforced thermoplastics. Carbon fiber composites have greater stiffness, higher fatigue endurance, and better wear characteristics than the corresponding glass fiber counterparts, but are not as tough, as exhibited by lower izod impact strengths. Carbon/glass hybrids provide average properties of the two reinforcements.

Addition of fibers to a melt greatly reduces shrinkage parallel to the direction of the fibers; however, the higher shrinkage in the transverse direction may result in severe warpage, as observed by Cloud, *et al.* (25). Warpage can be reduced by substituting a particulate filler for part of the reinforcing fibers. Any filler may be used (e.g., minerals, glass beads, milled fibers, etc.), but a substantial loss of properties is inevitable. Use of a platelet filler, such as mica, to improve upon anisotropic behavior of glass-fiber composites has been suggested by Maine and his coworkers (26, 27). Excellent stiffness and Young's modulus characteristics can be achieved with high-aspect-ratio mica. Inherent disadvantages of this filler are low impact strength, a loss of elongation, and processing limitations due to breakage of the flakes. A glass fiber/mica combination, however, offers excellent modulus and thermal characteristics, along with added strength and toughness due to glass fibers, as shown in *Table 5* for Nylon 6 composites. This particular combination of reinforcements is very suitable for large automotive parts.

Other applications may require combinations of carbon/glass/aramid reinforcements for the most cost effective performance.

POLYMER BLENDS

Rheological properties of two-phase polymer blends were studied by Han, *et al.* (18). A minimum in the viscosity vs. blending ratio was observed for polystyrene/polypropylene blends. Previous work on polystyrene/polyethylene blends (29) yielded similar conclusions.

Table 5. Comparison of Property Data for Glass Fiber/Mica Hybrid Against Mica Filled Nylon 6 Compound

Property	ASTM Method	Units	Nylon 6 15% Glass 25% Mica	Composites 40% Mica
Tensile Strength	D638	MPa	121.6	101.1
Tensile Modulus	D638	GPa	11.3	9.6
Elongation	D638	%	2.0	1.6
Flexural Strength	D790	MPa	184.2	168.3
Flexural Modulus	D790	GPa	11.6	10.6
Izod Impact Notched	D256	J/m	75.3	32.0
Izod Impact Unnotched	D256	J/m	500	267
HDT	D648	°C	190	190
Density	D792	g/cm³	1.49	1.48

Han expanded his study of these systems to include mechanical properties and found a minimum in the tensile strength vs. blending ratio graph (30).

These types of studies are of importance to the compounding industry, which uses a wide range of additives. Small amounts of HDPE have been used successfully in modifying the melt flow of reinforced polystyrene.

Rubber additives are, of course, of interest for impact resistance improvement, e.g., impact-modified ABS. Bouton reported on impact modifiers for polystyrene (31) and polypropylene (32). It is important to realize that a loss of other mechanical properties occurs.

In order to improve impact resistance of reinforced homo polypropylene, we have studied blending with coupled polypropylene. Izod impact vs. blending ratio is plotted in *Fig. 1*. As can be seen from the graph, the critical region is between 18 percent and 25 percent coupled PP, where most of the impact improvement occurs. Physical properties of the original polymers reinforced blends, and rubber modifiers are compared in *Table 6*. The compound containing 18 percent coupled polypropylene seems suitable for the plastic engine cooling fan, as described by Roth and his coworkers (33).

Table 4. Comparison of Dry Blending and Pre-Compounding for Coupled Polypropylene and Styrene Maleic Anhydride Copolymer

Property	ASTM Method	Units	Coupled PP	PP Dry Blend	PP Comp'd	SMA	SMA Dry Blend	SMA Comp'd
Tensile Strength	D638	MPa	20.8	62.2	50.7	40.3	88.3	85.3
Tensile Modulus	D638	GPa	—	4.6	—	—	7.2	7.4
Elongation	D638	%	—	2.9	—	—	1.5	1.5
Flexural Strength	D790	MPa	27.5	95.6	73.2	67.2	133	120
Flexural Modulus	D790	GPa	1.0	3.9	2.8	3.0	6.8	7.4
Flexural Modulus at 100°C	D790	GPa	0.3	1.2	0.9	1.7	—	—
HDT at 264 psi	D648	°C	44.7	137	107	90	110	115
Izod Impact Notched	D256	J/m	171	240	176	26	101	69
Izod Impact Unnotched	D256	J/m	2200+	427	450	170	283	211
% Glass	D2584	% w/w	0	20.6	18.2	0	20.3	20.6

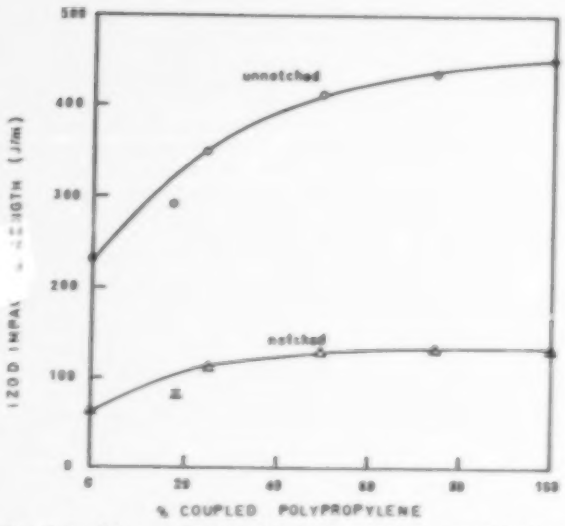

Fig. 1. Izod impact vs. blending ratio for homo/coupled polypropylene blends fortified with 30% glass fibers.

STRUCTURAL FOAM

There are obvious material and weight savings associated with the use of foamed (or blown) plastics. Part thickness limitations of structural foam (6 mm minimum) have been the biggest roadblock to resin savings (34, 35). Growth for structural foam is predicted in new markets, beyond the reach of rigid plastic molding technology.

If foam is to fully succeed, the benefits of fibrous reinforcement must be utilized. The role of glass fiber reinforcement is illustrated in *Table 7*, which summarizes the data on a foamed polyethylene part. As can be seen, reinforced foam has better mechanical properties than rigid resin and, surprisingly enough, the same density as unreinforced foam due to higher percent voids when glass fibers are present. Applications for this material are still being developed.

OTHER MOLDING PROCESSES

Thermoforming

Short-glass-fiber-reinforced HDPE sheet can be used in thermoforming, resulting in a reduction of up to 24 percent in resin requirements, 31 percent in heating time, and 14 percent in energy requirements compared to unreinforced HDPE sheet, reports Osborne (36). Analyses of the thermoforming process have also been presented by Osborne and his coworkers (37, 38).

Stamping

Modified metal stamping presses can be used to form fiberglass-reinforced thermoplastic sheet. Glass fibers are in a form of randomly oriented chopped strand mat. Productivity is high due to short cycles, as reported by Sikes (39).

Reinforced Reaction Injection Molding (RRIM)

RRIM is experiencing a tremendous growth due to a large market for automotive exterior parts: hoods, fenders, and deck lids. Milled glass fibers have been the preferred reinforcement, but new developments include chopped strands and flaked glass (40). Modifications of the existing process are required before the benefits of fibrous reinforcement can be fully utilized.

FUTURE TRENDS

Glass fibers are used to reinforce plastics primarily because of their excellent cost performance. Advanced fibers, although improving composite properties, are still not cost-effective for most applications, especially if tensile strength is important, since glass fibers provide three times as effective performance as aramid

Table 6. Comparison of Homo/Coupled Polypropylene Blends and Rubber Modifier in 30% Glass Fiber Fortified Compounds

Property	ASTM Method	Units	100% Homo Polymer	18% Coupled	50% Coupled	10% Elastomer	20% Elastomer
Tensile Strength	D638	MPa	33.3	65.8	69.5	—	—
Flexural Strength	D790	MPa	59.3	103.9	115.1	45.4	38.4
Flexural Modulus	D790	GPa	5.0	6.4	5.9	4.9	4.3
HDT at 264 psi	D648	°C	106	142	140	97	92
Izod Impact Notched	D256	J/m	64.0	89.4	128.1	170.8	235.3
Izod Impact Unnotched	D256	J/m	230	268	416.4	290	334.7
% Glass	D2584	% W	31.8	31.8	32.1	31.2	31.3

Table 7. Comparison of Properties of HDPE, 15% Glass Reinforced HDPE and their Performance in Foamed Part

Property	ASTM Method	Units	HDPE	HDPE 15% Glass	Foamed Part HDPE	Foamed Part HDPE 15% Glass
Tensile Strength	D638	MPa	18.7	41.9	16.7	23.0
Tensile Modulus	D638	GPa	—	3.35	0.97	1.74
Elongation	D638	%	—	6.7	8.8	5.8
Flexural Strength	D790	MPa	18.1	54.3	18.1	30.9
Flexural Modulus	D790	GPa	0.8	2.54	0.82	1.54
Solids	D2584	% w	0	15.9	0	14.8
Density	D792	g/cm³	0.96	1.07	0.88	0.90
Calculated % voids	—	% v	0	0	10	18

fibers (41). Most new applications will require an understandng of all types of reinforcements and their hybrids, thus providing unique new solutions.

Acceptance of short-fiber composites by the industry can largely be attributed to the ease of injection molding. When fully developed, RRIM should provide the same ease of processing in a new family of materials. The energy conservations aspects of glass-fiber reinforcement can not be overemphasized. The energy content of glass fibers is 66 MJ kg^{-1}, which is lower than even low-density polyethylene, the lowest plastic (42). From an energy conservation point of view, the most promising future growth can be expected for glass/polystyrene, glass/RIM urethane, BMC, glass ABS and glass/polypropylene. Of course, any new materials that provide the same kind of performance as existing, more energy-containing, materials will receive full attention.

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RETEC REPORT

Polyimides: Synthesis, Characterization and Applications

On November 10 to 12, 1982, the Mid-Hudson Section of the Society of Plastics Engineers will hold a Regional Technical Conference at the Nevele Country Club, in Ellenville, N.Y. Below is the program of presentations. Preprints of presentations will be available from SPE headquarters following the conclusion of the conference.

Synthetic Aspects

———— Synthesis and Characterization of Soluble Aromatic Polyimides—F. Harris, Wright State University.

———— Acetylene Substituted Polyimides—N. Bilow, Hughes Aircraft Co.

———— Modification of Polyimides by Incorporation of Silicone Blocks—A. Berger, M&T Chemical.

————V378A—A Modified Bismaleimide for Composites—S. Street, U.S. Polymerics.

————Water Soluble Polyimides—R. Pike, United Technologies.

———— Phosphorous-Containing Imide Resins: Modification by Elastomers—I. K. Varma, G. M. Fohlen, J. A. Parker, and D. Varma, NASA Ames Research Center.

————Polyetherimide: A Versatile Processable Thermoplastic—I. W. Serfaty, General Electric Co.

———— Synthesis and Properties of Ordered Copolyimides—S. Samant, I.I.T.

Properties and Characterization

———— Stress and Fatigue-Induced Molecular Phenomena in Polyimide Films—R. L. Levy, McDonnell Douglas.

———— Mechanical and Spectroscopic Properties of Metal Containing Polyimides—L. T. Taylor, VPI & SU and A. K. St. Clair, NASA Langley Research Center.

———— Mechanical Properties of Thin Polyimide Films—R. Lacombe, IBM.

———— Time-Temperature-Transformation (TTT) Cure Diagram for Reactive Systems—J. Gillham, Princeton University.

———— Etching of Partially Cured Polyimide—C. Diener and J. Susk, IBM.

———— The Cure Rheology of PMR Polyimide Resins—P. J. Dynes, T. T. Liao, C. L. Hamermesh, and E. F. Witucki, Rockwell International.

———— Characterization of Polyimides and Polyamic Acids in Dilute Solution—P. M. Cotts, IBM.

———— Elongation at Break as a Sensitive Probe for Polyimide Cure at High Temperature—M. Gupta, W. Weber, and H. Sachdev, IBM.

———— Structure-Property Relationships in Polyimides—M. Fryd, Du Pont.

———— Polyimide Protective Coatings for 700°F Service—R. J. Jones, G. E. Chang, S. H. Powell, and H. E. Green, TRW.

———— Sorption and Transport of Physically and Chemically Interacting Penetrants in Kapton Polyimide—L. Iler, W. J. Koros, D. K. Yang, and R. Yui, North Carolina State University.

———— Laser Micromachining of Polyimide Materials—P. Moskovitz, D. R. Vigliotti, and R. J. von Gutfeld, IBM.

————Evaluation of Polyimide Structural Adhesives for Extended Service—C. Hendricks, Boeing Co.

———— Dielectric and Chemical Characterization of the Polyimide, LARC-160—D. E. Kranbuehl, The College of William and Mary.

———— Thermally Stimulated Discharge Currents from Corona Charged Polypyromellitimide Film—J. K. Quamara, P.K.C. Pillai, Indian Institute of Technology; B. L. Sharma, Regional Engineering College.

Interfacial Aspects

————The Inner Layer Adhesion of Polyimide Multilayer Printing Wiring Boards—T. E. Baker, Raytheon.

———— Novel Method for Electroless Metallization of Polyimides: Topochemical Oxidative Decomposition of Highly Reduced Metal Clusters—R. Haushalter and L. J. Krause, Argonne National Laboratory.

————The Modification of Polyamic Acids with γ-Aminopropyltriethoxysilane and the Characterization of the Reaction Product—L. Minnema and J. M. van der Zande, Philips.

———— Mechanistic Implications of the Use of 3-Aminopropyltriethoxysilane as Adhesion Promoter for Polyimides—J. Greenblatt, C. J. Araps, and H. R. Anderson Jr., IBM.

———— Metalized and Plasma Etched Polyimide Surfaces—H. Leary and D. S. Campbell, IBM.

Microelectronic Applications

————Use of Polyimides in VLSI Fabrication—A. Wilson, Texas Instruments.

————Polyimide Patterns Made Directly from Photopolymers—H. Ahne, H. Kruger, E. Pammer, and R. Rubner, Siemens.

———— Techniques for Improving Packaging Density in a Polyimide Multilevel Metallization Process—S. J. Rhodes, Plessey Research (Caswell).

———— Intermetal-Polyimide Via Conditioning and Plasma Etching Techniques—T. O. Herndon, R. L. Burke, and W. L. Landoch, M.I.T. Lincoln Laboratory.

————Polyimide Planarization in Integrated Circuits—D. R. Day, D. Riley, J. Mario, and S. D. Senturia, M.I.T.

————Fine Pattern Processes for Polyimide Insulation—A. Saiki, K. Mukai, T. Nishida, H. Suzuki, and D. Makino, Hitachi.

————Polyimide Chemistry and Its Relations to Microelectronic Application—Wagner, Siemens.

———— Reliability of Polyimide in Semiconductor Devices—G. Samuelson and S. Lytle, Motorola.

Aerospace and Other Applications

———— PMR Polyimide Composites for Aerospace Applications—T. Serafini, NASA Lewis Research Center.

———— Polyimide Composites—L. Poveromo, Grumman Aerospace.

———— The Development of Aerospace Polyimide Adhesives—T. L. St. Clair and A. K. St. Clair, NASA Langley Research Center.

———— Electrophoretic Deposition of Polyimides: An Overview—L. C. Scala, W. M. Alvino, and T. J. Fuller, Westinghouse.

———— Polyimide: Tribological Properties and Their Use as Lubricants—R. L. Fusaro, NASA Lewis Research Center.

———— Polyimide Adhesives for LSI/VLSI Hermetic Packages—J. C. Bolger, Amicon Corp.

———— Polyimides as Insulating Layers for Implantable Electrodes—H. K. Charles Jr., J. T. Massey, and V. B. Mountcastle, Johns Hopkins University.

———— New Developments in Photosensitive Polyimides—H. J. Merrem, Merck.

———— Polyimide Blends—J. Adduci, Rochester Institute of Technology.

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   Maximum credits allowable for education shall be six (6). Use highest degree credits ONLY

Doctorate in science or engineering	**6 credits**
Masters in science or engineering	**5 credits**
Bachelors in science or engineering	**4 credits**
Any degree other than above	**2 credits**
Associate or Adjunct in Plastics	**2 credits**
Associate or Adjunct (awarded by Community College or equivalent for two-year course of studies, without specializing in plastics).	**1 credit**

When filling in the "Statement of College Work" above, place the corresponding number of credits earned in the right-hand column

2. **Experience credits** are determined by the proportion of time involved in actual technical and engineering duties in plastics for each position held. For instance, if only three of the five years you worked for the XYZ Co. comprised technical or engineering duties, then three (3) years (60% of 5 yrs.) would constitute the "Qualifying Experience" you would enter in years and months in the right-hand column under "Record of Qualifying Experience in Plastics."

   Please detail carefully the engineering skill required for each position to help the Credentials Committee judge experience as "qualifying."

When you have determined the number of credits which you believe you have earned, consult the following member grade requirements. Indicate on the reverse side the grade of membership for which you believe you are qualified.

INFORMATION FOR AUTHORS

Submission of original and review articles is encouraged. There is no limit on length. Three copies of the manuscript should be submitted, which should be typed, one side only, double space, with at least a 1-inch margin. Submission will be taken to imply that the paper has not been previously published, that it is not being considered elsewhere for publication, and that if accepted it will not be published elsewhere in the same form, in any language, without the consent of the editor or publisher. Authors must agree to transfer copyright to the publisher when an article is accepted for publication. Unless notified to the contrary by the authors, the publisher assumes that the act of submitting the article signifies the author's agreement to such copyright transfer to the publisher. The journal carries a voluntary page charge. Each manuscript should include:

A separate title page, headed by a concise, meaningful title (avoid abbreviations) for the paper. This page should provide:

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A separate abstract page, consisting of a single paragraph of 100-200 words to include the title and the names and addresses of the authors. Define any abbreviations for substances or methods (such as ABS, SAXS, etc.).

A list of references, on a separate page at the end of the text, numbered in order of text citation. The references are to be abbreviated in the form used in Chemical Abstracts using the names of all authors preceded by initials; see Bibliographic Guide for Editors and Authors, American Chemical Society, Washington, D.C.

- Within the text, the reference citations are typed in parentheses in line with the main copy (no superscripts or subscripts), thus:

  According to Young, et al (1).

- In the list of references the general style is as follows:

For periodicals:

1. S. S. Young, J. L. White, E. S. Clark and Y. Oyanogi, Polym. Eng. Sci., 20, 798 (1980).

The journal name and volume are to be underlined and the year is placed in brackets. The issue number is given only when needed for identification. The article name is eliminated unless the reference is unclear without it.

For books: The title to be spelled out in full.

5. H.-G. Elias, "Macromolecules," Ch. 1, Vol. 2, Plenum Press, New York (1977). (Include the state when the city is not identifiable.)

A list of nomenclature, identifying symbols and abbreviations, commonly desirable at the end of the text. Footnotes are to be avoided.

Equations, numbered and typed in the appropriate place in the text. Where symbols cannot be typed, write them neatly in ink.

Tables, each typed on a separate page, with a heading, and numbered with arabic numerals that correspond to the order in which they are cited in the text. The tables should be inserted in the manuscript after the references and before the figures.

Figures, assembled at the end of the manuscript and preceded by a typed list of captions that explain them. Please also supply a set of original figures or sharp glossy photos thereof, on 8½ × 11 paper or attached to sheets of this size, one sheet for each figure. Each should be identified on the front edge or on the back (photographs) with the name of the first author and the figure number (e.g., Smith, Fig. 1). Originals are to be prepared with high contrast India ink and to bear uniformly stencilled notations. Line drawings and photos should be of a quality suitable for good photographic reproduction and retained legibility upon size reduction to one quarter. Manuscript transmittal letter should indicate if the figures need be returned.

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